Comets are regarded as probably the most primitive of solar system objects, preserving a record of the materials from which the solar system aggregated. Key amongst their components are organic compounds – molecules that may trace their heritage to the interstellar medium from which the protosolar nebula eventually emerged. The most recent cometary space mission, Rosetta, carried instruments designed to characterize, in unprecedented detail, the organic species in comet 67P/Churyumov–Gerasimenko (67P). Rosetta was the first mission to match orbits with a comet and follow its evolution over time, and also the first mission to land scientific instruments on a comet surface. Results from the mission revealed a greater variety of molecules than previously identified and indicated that 67P contained both primitive and processed organic entities.

**Keywords:** Rosetta, comet, chemistry, organics, volatiles, isotopes

### OVERVIEW

Rosetta was the third of four Cornerstone missions of the European Space Agency’s (ESA’s) Horizon 2000 program. It was launched 2 March 2004. Rosetta followed a 10-year journey that included fly-by of the asteroids (2867) Steins [5 September 2008] and (21) Lutetia [10 July 2010], and caught up with comet 67P/Churyumov–Gerasimenko (hereafter, 67P) on 6 August 2014 (Fig. 1). The spacecraft kept station with the comet for three months, mapping the surface of the nucleus and taking measurements of the dust and ice released into the coma. On 12 November 2014, a lander, Philae, was released from Rosetta onto the surface of 67P.

Unfortunately, a series of technical malfunctions resulted in a less than perfect landing for Philae, was released from comet 67P/Churyumov–Gerasimenko (hereafter, 67P) on 6 August 2014 ([Fig. 1](#)). The spacecraft kept station with the comet for three months, mapping the surface of the nucleus and taking measurements of the dust and ice released into the coma. On 12 November 2014, a lander, Philae, was released from Rosetta onto the surface of 67P.

The Rosetta spacecraft continued to fly alongside 67P as the comet went through perihelion (the closest point to the Sun, 13 August 2015); the distance between Rosetta and the comet increased to around 340 km at solar approach and return, but then decreased to between 50–100 km for the rest of the mission, occasionally dropping to a height of ~10 km. The mission ended 30 September 2016 when Rosetta performed a controlled glide onto the surface of 67P.

The Rosetta spacecraft and the Philae lander carried a variety of instruments to cover almost all aspects of investigation of a cometary nucleus (its solid body) and coma (its cloud of gas and dust). This paper will focus on the chemistry of the dust and volatile organic species in comet 67P and consider results that were obtained by direct analysis of specific molecules. Findings derived from imaging or spectroscopic measurements will not be presented. The volatile chemistry of comets prior to the Rosetta mission are described by Brownlee et al. (2018 this issue) and Yabuta et al. (2018 this issue). The analytical results came from scientific instruments called COSIMA (a secondary ion mass spectrometer) and ROSINA (a combined double-focusing mass spectrometer reflexion time-of-flight detector) on the main Rosetta spacecraft, as well as from COSAC and Ptolemy (both variants of gas chromatograph and mass spectrometer systems) which were taken down to the surface of the comet on board the Philae lander.
COMET 67P/CHURYUMOV–GERASIMENKO
A further era of cometary investigation started with the Rosetta space mission to 67P/Churyumov–Gerasimenko. Rosetta was the first space mission to travel alongside a cometary nucleus as it moved through perihelion. This enabled the spacecraft to observe changes in the comet’s activity and associated modifications to its landscape (El-Maarry et al. 2017). The Rosetta spacecraft included instruments that identified the composition and abundance of coma gases and particles released from the surface. There were also instruments that made spectroscopic measurements of the surface of 67P and the cloud of coma gases surrounding the comet. Instruments on-board the Philae lander took measurements directly on the comet’s surface, allowing comparison between analytical measurements of chemical compositions made directly on the nucleus with results made by instruments on-board the orbiting Rosetta spacecraft.

Specific observations on the physical nature of the comet give context to the chemistry of 67P. The comet is very dark, with an albedo of 0.06, implying that ice is rare at the surface (Fornasier et al. 2015). This comet is also highly porous (~75%), with an overall density of 500 kg m\(^{-3}\), even though images appear to show a solid-looking object. The overall dust-to-gas ratio in 67P is about 10 to 20 (by mass), and the dust is thought to contain ice, minerals and organics. The non-icy portion of the dust contains ~55% weight percent of minerals and ~45% of organics (Bardyn et al. 2017). According to Fulle et al. (2016), the density of the particles would be compatible with 15 ± 6% ices, 5 ± 2% Fe-sulfides, 28 ± 5% silicates, and 52 ± 12% organic species (by volume). The dust occurs in fluffly and compact particles, as seen by the three dust instruments (GIADA, MIDAS and COSIMA), with estimated densities that can vary from very low values (<1 kg m\(^{-3}\)) to densities around 3,000 kg m\(^{-3}\) for compact particles (Fulle et al. 2016; Hornung et al. 2016; Langevin et al. 2016; Merouane et al. 2017).

The (surface) temperature of a comet changes during progress around its orbit. During the Rosetta encounter with 67P, the temperature increased from about –70 °C at 3.5 AU (astronomical unit, the average Earth–Sun distance) to values higher than freezing at perihelion (~1.25 AU), with the hottest temperature around +80 °C. A result of this elevated temperature is that during the encounter, ices would sublime, giving rise to species such as H\(_2\)O, whilst the dusty components could have been lofted into space (to be detected by instruments like GIADA or MIDAS, or collected and analysed by COSIMA). For 67P, at 2.9 AU, a total of approximately 15 kg of dust was being lost per second, compared with 3.5 kg of (water) ice. On top of the orbital cycle, there is a daily thermal cycle at the cometary surface that causes sublimation of ice, some of which is irreversibly lost from the comet and some concentrated by migration deeper into the colder surface (Filacchione et al. 2016). This mechanism complicates assessment of the overall dust/gas ratio of the nucleus.

VOLATILE AND DUST CHEMISTRY OF COMET 67P FROM ROSETTA

Dust in the Coma
COSIMA (COmetary Secondary Ion Mass Analyser) was one of three dust instruments on board the Rosetta orbiter, together with MIDAS and GIADA, and was the only one of the three that measured the composition of the dust. During the 26 month mission, COSIMA detected more than 30,000 dust particles (or fragments thereof) with sizes from 800 µm down to the resolution (14 µm × 14 µm) of the camera (COSISCOPE). The measured dust flux at high phase angle (the angle made between Sun–comet–Rosetta), follows a 1/d\(^2\) law, where \(d\) is the nucleocentric distance; at low phase angle, the dust flux was more dispersed...
The dust particles, classified either as compact or porous aggregates (Langevin et al. 2016), were collected at low speeds, less than ~10 m·s⁻¹ (Rotundi et al. 2015). On previous missions (e.g. Stardust), dust collection occurred at speeds of several km·s⁻¹, so in comparison, the 67P grains were relatively unaltered (Merouane et al. 2017 and references therein). The particles collected by COSIMA exhibited a fluffier to porous morphology similar to interplanetary dust particles and micrometeorites, and most of them fragmented upon collection (Langevin et al. 2016), suggesting a relatively low dense strength, estimated at 1–2 MPa (Hornung et al. 2016). It is significant that analysis of aerogel from the Stardust mission also provided evidence for weak and strong particles. The weak ones produced very bulbous capture tracks filled with diverse materials, while the strong ones produced tracks like thin carrots and were usually composed of only one type of material (Brownlee 2014).

About 200 of the collected particles with a size range of 15–225 μm were analysed by COSIMA using a time-of-flight secondary ion mass spectrometer. The instrument measures secondary ions ejected from the surface of a grain when it is bombarded with 8 keV positive iodium ions. The elemental composition of dust particles of comet 67P, as measured by COSIMA, show that their bulk composition is compatible within a factor of three with chondritic abundances, except for carbon, which is >5 times higher in 67P (Hilchenbach et al. 2016; Bardyn et al. 2017). The average Na/Mg ratio is significantly higher than the CI [Ivuna-type carbonaceous meteorite] composition, Na being enriched relative to CI chondrite whereas Mg is depleted (Schulz et al. 2015; Bardyn et al. 2017). The host phase for Na and the cause of the Mg depletions are not yet known. There is compositional evidence for the presence of at least one Ca–Al-rich particle analysed by COSIMA to date (Paquette et al. 2016).

The high carbon content detected by COSIMA in 67P dust is attributed to the presence of a large abundance of high molecular-weight organic matter in the collected dust particles (Fray et al. and the cause of shares spectral similarities with insoluble organic matter extracted from carbonaceous chondrites, and has a comparable average N/C atomic ratio of 0.04 ± 0.01 (Fray et al. 2017). Although this could possibly indicate a common origin or formation process for the organic matter in carbonaceous chondrites and 67P, the organic matter in 67P seems less altered (with higher H/C ratio) than meteoritic insoluble organic matter. This suggests less processing of the comet compared to the parent bodies of meteorites. The morphology of the 67P particles, as well as their compositions, point toward a similarity with interplanetary dust particles collected in the stratosphere by NASA and with micrometeorites recovered from polar snow and ices (Hilchenbach et al. 2016; Langevin et al. 2016).

**Gases in the Coma and the Cometary Zoo**

Gases in the coma of comet 67P were measured by the ROSINA instrument (Rosetta orbiter spectrometer for ion and neutral analysis), which has identified an impressive array of molecules in the coma gases. The list has grown over time as more results have been processed and is likely to grow further. Relevant data can be found in a range of sources, e.g. Le Roy et al. (2015). An up-to-date overview of the understanding of coma chemistry, largely based on ROSINA data, is given by Altwegg et al. (2017). A key measurement from ROSINA was determination of the D/H of water in the coma gases of 67P (Altwegg et al. 2015). At 5.3 ± 0.7 × 10⁻⁴, the coma water is about three times as enriched in deuterium as water in the Earth’s oceans (D/H = 1.6 × 10⁻⁴). Not only that, but the result showed that variation in D/H of Jupiter-family comets was much greater than previously suspected, meaning that the D/H ratio of a comet can no longer be used as a discriminator between Jupiter-family comets and long-period comets.

One of the most surprising results from ROSINA was the detection of molecular oxygen (Bieler et al. 2015), not at trace levels, but up to 10% relative to the major component, water. The abundance did not appear to change as the comet drew closer to the Sun, implying that it was distributed homogeneously throughout the nucleus. The only way that this could be true is if the oxygen had been incorporated into the comet when it formed in the pre-solar nebula. Oxygen gas is a very reactive species and is not usually considered as being present in abundance in the outer part of the protoplanetary disk. Oxygen was assumed to have occurred as water, CO, or CO₂, so the observation of O₂ poses interesting constraints on solar system formation processes. The oxygen story is also important because, until relatively recently, the presence of oxygen in a planetary atmosphere was thought likely to be an indicator of the presence of life. There is, however, no suggestion that comets, including 67P, harbour life – but they are clearly the carriers of some of the chemical precursors for life.

The ever-growing list of molecules identified by ROSINA has resulted in the notion of a “cometary zoo” of atoms and molecules (Fig. 3), introduced by Kathrin Altwegg (ROSINA Principal Investigator). The cometary zoo is arranged such that molecules with similar properties have been grouped together and are assigned to a specific animal as an aide memoir. For example, cyanogens are difficult to identify and were placed in the chameleon group. See Table 1 for more examples.

The double-focusing mass spectrometer component of ROSINA has a high mass resolution and can distinguish between species with very similar masses, e.g. ¹²C¹⁹O (molecular mass of 27.9949) and that of ¹⁴N¹¹N (molecular mass of 28.0062). Although it would have been useful to have had a second version of ROSINA on the surface of 67P, that was not practicable because the physical size and mass of ROSINA was too great to transport the instrument to the surface of 67P on Philae. Also, ROSINA’s mode of operation – continuous monitoring of the gas species – is unsuitable for an investigation that was intended to collect samples of solid materials from the surface of 67P. Hence, different instruments were provided to determine the chemistry of the cometary surface.

**Measurements at the Surface of 67P**

The COSAC and Ptolemy instruments on Philae had masses of a few kilograms each and were colloquially described as being shoe-box-sized. Both instruments employed gas chromatography, coupled with incremental heating, to effect partial or complete separation of species, thereby enabling a distinction to be made between molecules with closely matched molecular masses. However, the instruments were designed to have unit mass resolution across their operating ranges of 10–200 atomic masses; because this mass resolution was lower than that of ROSINA, it precluded direct resolution of ¹²C¹⁹O from ¹⁴N¹¹N.

It had been intended that samples retrieved by Philae’s drill would be placed in an oven for subsequent processing and analysis, but the awkward circumstances of Philae’s landing meant that such experiments were not possible. Because the lander was on its side, the drill was too far away from the surface to make contact and collect a sample. No surface sample could be deposited in any of the ovens and so it was not possible to use these capabilities of either COSAC...
or Ptolemy. However, both COSAC and Ptolemy could function in “sniffing mode”, where ambient gas species passed straight into the detector, an operational mode akin to that of the ROSINA mass spectrometer on the *Rosetta* orbiter. Both COSAC and Ptolemy were scheduled to be operating at the time of touchdown at Agilkia (the first point of contact with the comet) and both acquired data throughout the 5-hour time interval before *Philae* came to rest.

The results from Agilkia obtained by COSAC and Ptolemy were published by Goesmann et al. (2015) and Wright et al. (2015), respectively, and revised in Altwegg et al. (2017). Representative spectra from the two instruments are shown in Figure 4, in which, despite differences in the operational modes of COSAC and Ptolemy, the two systems recorded results that were similar overall, but different in detail. The two teams also interpreted their results differently. Wright et al. (2015) inferred from the Ptolemy data that, once the major features from H$_2$O and CO$_2$ were stripped away, the main peaks remaining in the spectrum came from the breakdown of the CHO-bearing polymer that is polyoxy-methylene, (CH$_2$O)$_n$.

Wright et al. (2015) commented on the low abundance of nitrogen-bearing species, suggesting that features in the Ptolemy spectrum that could be associated with NH$_2$OH (hydroxylamine; m/z = 33) and CH$_3$CN (isocyanomethane; m/z = 41) were more likely to be from hydrocarbon fragments with the same mass. In contrast,

![The Cometary Zoo: Gases Detected by Rosetta](image)

**Figure 3** The cometary zoo. A light-hearted classification of the different species found in the coma of 67P. The data are based on the findings of the ROSINA instrument.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>The Cometary Zoo of Gases Detected by Rosetta</th>
</tr>
</thead>
<tbody>
<tr>
<td>Animal</td>
<td>Characteristic</td>
</tr>
<tr>
<td>butterfly</td>
<td>volatile</td>
</tr>
<tr>
<td>peacock</td>
<td>Beautiful and solitary</td>
</tr>
<tr>
<td>oyster</td>
<td>hard shell</td>
</tr>
<tr>
<td>fish</td>
<td>salty</td>
</tr>
<tr>
<td>giraffe</td>
<td>long carbon chains</td>
</tr>
<tr>
<td>snake</td>
<td>poisonous</td>
</tr>
<tr>
<td>monkey</td>
<td>spirited</td>
</tr>
<tr>
<td>skunk</td>
<td>smelly</td>
</tr>
<tr>
<td>frog</td>
<td>smelly &amp; colourful</td>
</tr>
<tr>
<td>zebra</td>
<td>smell of manure</td>
</tr>
<tr>
<td>bird</td>
<td>exotic molecules</td>
</tr>
<tr>
<td>elephant</td>
<td>heavy</td>
</tr>
<tr>
<td>lion</td>
<td>king of the zoo</td>
</tr>
<tr>
<td>chameleon</td>
<td>difficult to identify</td>
</tr>
</tbody>
</table>
Goessmann et al. (2015) identified a wide variety of organic molecules in low abundance compared to water, including CH$_3$CHO (ethanal, also known as acetaldehyde); CH$_2$OHCHO (2-hydroxyethanal) and CH$_2$(OH)CH$_2$(OH) (1,2-ethanediol). The presence of nitrogen-bearing species – including CH$_3$NH$_2$ (methylamine), C$_2$H$_5$NH$_2$ (ethamine), HCONH$_2$ (methylamidine), plus several molecules not identified previously in comets, such as CH$_3$NCO (isocyanatomethane), CH$_3$COCH$_3$ (propanone), C$_2$H$_5$CHO (propanal) and CH$_3$CONH$_2$ (ethanamide) – were inferred from the spectrum. Both COSAC and Ptolemy teams noted the absence of sulfur-bearing molecules.

Altwegg et al. (2017) compared the COSAC and Ptolemy data acquired at the surface of 67P at Agilkia with the ROSINA results taken from coma gases whilst in orbit around the comet. The mass spectra of all three instruments showed very similar patterns of mainly CHO-bearing and CHON-bearing saturated and unsaturated species present. The signature of the aromatic compound toluene (m/z = 92) was identified in both the ROSINA and Ptolemy data. Re-evaluation of the COSAC mass spectra failed to confirm the presence of isocyanatomethane, propanal, and 2-hydroxyethanal. Similarly, the presence of polyoxymethylene in the Ptolemy mass spectrum was rejected.

A major significance of the COSAC and Ptolemy data is that many of the molecules detected in the coma gases by ROSINA were not detected at the surface of the comet. Because the coma gases emanate from jets sampling sub-surface materials, it is possible that some of the molecules detected by ROSINA (e.g. pentane, hexane, and others) were modified by irradiation or thermal cycling at the surface and were, therefore, not present in the materials sampled by COSAC and Ptolemy. And because irradiation can act to polymerise or aromatize small molecules to form larger, polyaromatic, compounds, it could be these that give the surface of 67P (and, indeed, other comets) its dark colour. The question then becomes: did these polyaromatic compounds form early in the life of the comet, or were they formed at the surface by irradiation?

**SUMMARY: IS ANOTHER COMET MISSION REQUIRED?**

The inventory of organic volatiles in 67P provides a starting point for further investigations of solar system processes, including cometary formation and development. We are starting to make connections between the results from the Rosetta mission with specific extraterrestrial materials available for study on Earth (e.g. carbonaceous chondrites and interplanetary dust particles). This is not a straightforward comparison: the nature of the instrumentation on-board Rosetta and Philae, coupled with Philae’s unfortunate landing meant that only volatile organic species have been measured in depth. There still has not been a detailed study of the more refractory organic compounds that almost certainly comprise a large proportion of the organic inventory of comets. Carbonaceous chondrites of the CI, CM and CR types contain up to 5 wt% C and 20 wt% H$_2$O. The carbon is present in a range of organic compounds, broadly speaking as ~20% of “soluble” species (small, volatile molecules) and ~80% of “insoluble” species (complex macromolecular structures of cross-linked entities forming a net-like assemblage). Structural and compositional analysis of meteoritic organic species, alongside high-precision isotopic measurements, help to constrain sources or formation conditions. But a direct comparison between meteoritic organics and organic molecules detected in comets is difficult because the survival of such materials in meteorites that arrive on Earth is unlikely. Water in carbonaceous chondrites is combined within phyllosilicates minerals and organic molecules, rather than as H$_2$O ice, as is the case in comets. Having said this, the high proportions of organic compounds and “water” in both carbonaceous chondrites and comets clearly points to some kind of relationship.

So, there is a mismatch in the materials available for study: we have analysed volatile organic compounds in detail in comets, but not the refractory organics. Meteorites contain volatile and refractory organics, both populations of which have been investigated, but meteorites lose the most volatile of materials, including the ices and trapped gases that occur in abundance in comets.

Despite the success of Rosetta and Philae, we still do not have a good understanding of the inventory of soluble pre-biotic organic compounds in comets. The future is quite clear: we need a comet nucleus sample-return. At the time of writing, the NASA process for selecting the fourth mission in the New Frontiers program is in progress, and the CAESAR cometary mission to 67P is one of the two missions selected for further development. If CAESAR is triumphant at the end of the process, then we may have cometary volatiles collected directly from comet 67P back on Earth in 20 years’ time!

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REFERENCES


Fornasier S and 53 coauthors (2015) Spectrophotometric properties of the nucleus of comet 67P/ Churyumov–Gerasimenko from the OSIRIS instrument onboard the ROSETTA spacecraft. Astronomy and Astrophysics 583, doi: 10.1051/0004-6361/201525901

Le Roy L and 17 coauthors (2015) Inventory of the volatiles on comet 67P/ Churyumov-Gerasimenko from Rosetta/ROSINA. Astronomy and Astrophysics 583, doi: 10.1051/0004-6361/201526450


Hornung K and 11 coauthors (2016) A first assessment of the strength of cometary particles collected in situ by the COSIMA instrument onboard ROSETTA. Planetary and Space Science 133: 63-75

Langevin Y and 10 coauthors (2016) Typology of dust particles collected by the COSIMA mass spectrometer in the inner coma of 67P/ Churyumov Gerasimenko. Icarus 271: 76-97


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