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

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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.

The study of the chemical composition of comets provides key information about the raw materials present in the early solar system ([1], [2]). Ground and space-based observations have identified over 20 organic molecules in comet comae ([3], [4]), a subset of which are of prebiotic interest ([5], [6]).
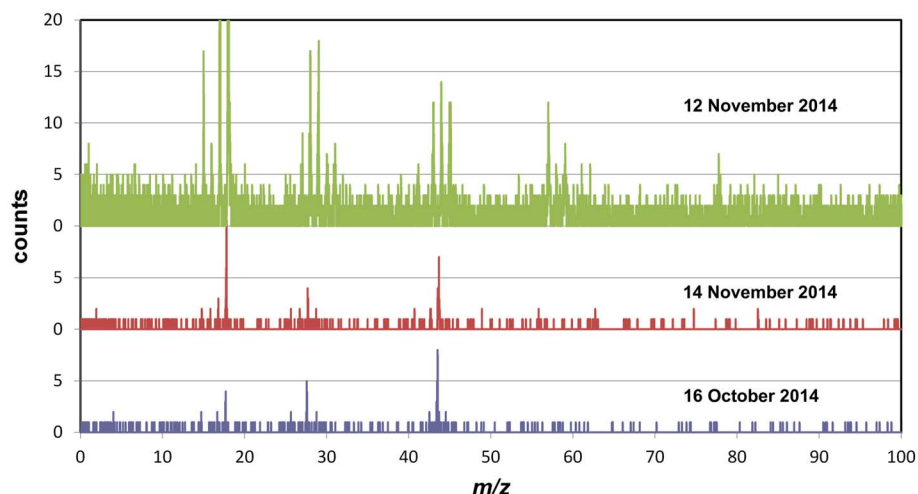
The Cometary Sampling and Composition (COSAC) experiment on Rosetta's lander Philae was designed to detect and identify organic molecules in the material of comet 67P ([7]). It consists of a gas chromatograph (GC) and a time-of-flight mass spectrometer (TOF-MS) to analyze samples delivered by the sample drilling and distribution system (SD2). COSAC can also operate in sniffing mode, in which the MS accumulates data without active sampling by SD2. Molecules that have passively entered the instrument are ionized, accelerated, and finally registered by COSAC. MS sniffings were made several times between launch and arrival at the comet, including during a fly-by of Lutetia ([8]). MS sniffings were made on arrival at 67P from 10 km above the surface, after initial touchdown, and at the final resting site (Fig. 1).

The Philae lander first touched down on 67P on 12 November 2014 at 15:34:04 UTC and then bounced. The impact excavated about 0.4 m³ of solid material ([9]), some of which would have entered COSAC's two exhaust pipes, which are on the bottom of the lander ([10]), and then stuck to the inside of the 2-cm-wide pipes. The temperature in these pipes was 12° to 15°C ([10]), midway between the cold cometary exterior and the heated interior of the lander, allowing volatile organics to sublime and be detected by the MS in a measurement that began at 16:00:30 UTC and ended at 16:02:50 UTC, when the lander was about 150 m above the surface on its first bounce. We focus here on this spectrum (green in Fig. 1), which differs fundamentally in the number and intensity of its peaks from the undisturbed spectra taken before and after, and represents excavated cometary material ([10]). Our approach was to find the best fit to this spectrum of a superposition of standard National Institute of Standards and Technology (NIST) mass spectra ([11]) of candidate cometary molecules. The spectral deconvolution methodology used is similar to that used in other space missions [such as the Ion and Neutral Mass Spectrometer (INMS) measurements by Cassini and the GCMS on the Huygens probe] ([12]–[14]).

Because COSAC has a mass resolution of only 300, single mass peaks cannot be resolved into different molecular species [e.g., CO, N_2, and C_2H_4, all at a mass/charge ratio (m/z) of 28, are indistinguishable]. Analysis ([10]) was limited to compounds below m/z 62 because signals beyond this value are too faint to be distinguished reliably from noise. The peak at m/z 78, for example, is not real: Several ions coincidentally ended up in a single channel, leaving neighboring ones empty ([10]). All conceivable molecules were first listed and their fragmentation patterns evaluated (table S1). Elimination of molecules with incompatible fragmentation patterns (for reasons described in table S3) led to a short-list of candidate molecules (table S2). We further reduced the short list by making the fit in order of decreasing mass,

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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.

starting from m/z 59 (*10*), and eliminating unstable and unsaturated species. This yielded a good fit to all peaks (except m/z 15 and a fraction of m/z 29, Fig. 2) with 16 species from several families of molecules—alcohols, carbonyls, amines, nitriles, amides, and isocyanates—in a consistent combination (Table 1). Peaks for $m/z < 10$ were not included in the fit because they are not listed in the standard NIST mass spectra (*11*). The molecular abundances of these compounds relative to that of water (Table 1) were corrected for electron cross section (table S4). The absence of ions at m/z 32 indicates a lack of sulfur-bearing species (Fig. 2 and Table 1). Amino acids were not included in the fit because the molecular ion peaks of glycine (m/z 75) and alanine (m/z 89) are negative after background subtraction, thereby suggesting that they are noise. Although fragment peaks assigned to glycine and alanine in the NIST standard spectra (*11*) are present in the COSAC spectrum (in the m/z 30s to 40s range), any contribution to these fragment peaks from amino acids is difficult to disentangle from the contributions of other species.

The main source of error is the low signal intensity, averaging about 100 counts (table S1). A statistical square-root of n approach yields a standard deviation of 10%. In addition, the NIST standard spectra (*11*) have a 15% error. Considering formal error propagation and the uncertainties in our peak-fitting algorithm, we estimate that the abundances given in Table 1 are accurate to about a factor of 2. The fit of a mass spectrum whose peaks result from the superposition of different molecular species is intrinsically degenerate, with several possible solutions (*10*).

The absence of large quantities of NH_3, HCHO, and CO_2 in our best fit may seem surprising because they were expected to be present as components of cometary ice. NH_3 (m/z 17) was not needed for the fit, but the presence of small quantities seems likely. However, this is hard to quantify because the large H_2O peak at m/z 18 implies a substantial contribution to the m/z 17 peak from the OH fragment peak of H_2O, which is difficult to distinguish from any NH_3 contribution. HCHO (m/z 30) and CO_2 (m/z 44) are not included because m/z 30 is mainly accounted for by fragment peaks of other molecules, rather than by the molecular ion of HCHO, and m/z 44 is mainly accounted for by fragment contributions from acetamide, formamide, and acetaldehyde, rather than by CO_2.

We initially tried a fit that started with the assumption that m/z 44 came from CO_2, but no acceptable fit could be achieved for the remaining peaks. If all of m/z 44 were ascribed to CO_2, our sample would only contain 3% of CO_2 relative to water. Using the procedure described above, we found that a more sensible fit for all mass peaks, especially m/z 57, 58, and 59, could only be achieved by assuming a CO_2 concentration of less than 0.1%. The low abundance of CO_2, NH_3, and HCHO could indicate that the excavated COSAC sample came from an area depleted in volatile ice components. Observations by the Visible, Infrared and Thermal Imaging Spectrometer

(VIRTIS) from the Rosetta orbiter (*15*) do suggest a dark surface depleted in volatiles, consisting mainly of refractory organic macromolecular materials, with very little ice on the surface. Studies (*16*) using the Rosetta Orbiter Spectrometer for Ion and Neutral Analysis (ROSINA) indicate that

volatile ices sublime diurnally and seasonally, with CO_2 ranging from 3% relative to water in local summer (the present case) to 80% in local winter.

The COSAC findings differ from those of Ptolemy (*17*) because COSAC sampled particles excavated by the impact (*10*) that entered the warm

Fig. 2. The fit to the observed spectrum. Comparison of the COSAC original mass spectrum (black bars for each integer mass) and the spectrum reconstructed from the best fit (orange bars to right of original signal). The peak heights are normalized to 100 for the m/z 18 peak (which has been truncated).
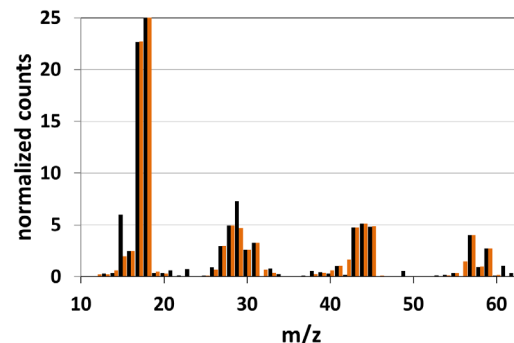
Table 1. The 16 molecules used to fit the COSAC mass spectrum.

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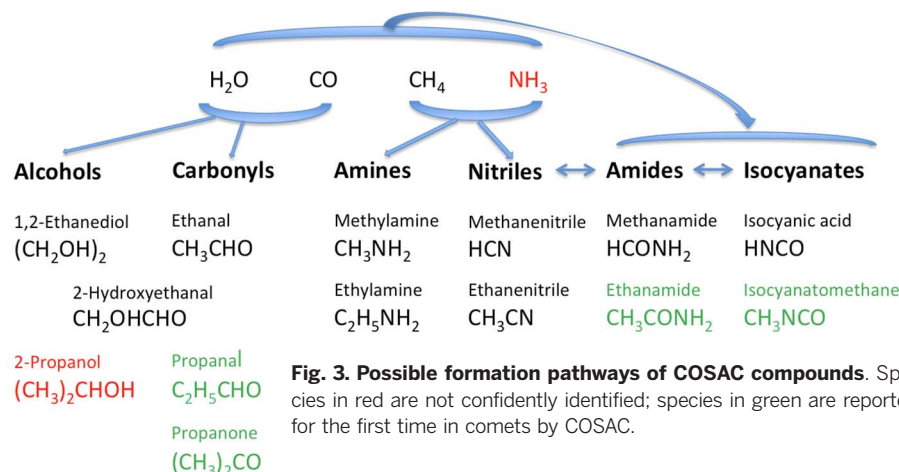
Fig. 3. Possible formation pathways of COSAC compounds. Species in red are not confidently identified; species in green are reported for the first time in comets by COSAC.

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. After sublimation, the total pressure inside the COSAC MS was due to the sum of the partial pressures of all the sublimed ground materials. This can explain the missing CO_2 in the post-touchdown spectrum. The displacement of ambient coma gases by subliming ground materials and the temperature of 12° to 15°C in the COSAC exhaust tubes, which is too low to break down any refractory polymers in the ground materials, combine to explain why COSAC did not detect any polymer fragments.

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.

Several of the COSAC compounds, such as HCN, CH_3CN, and HNCO, are present in the comae of most comets ([1]). Others, such as CH_3CHO, $HCONH_2$, $CH_2(OH)CH_2(OH)$, CH_3NH_2, and $C_2H_5NH_2$, have only been found in a few comets. Four molecules reported by COSAC—CH_3NCO, CH_3COCH_3, C_2H_5CHO, and CH_3CONH_2—have not been previously reported in a cometary environment, and

CH_2OHCHO has only been reported as an upper limit. These cometary molecules are all predicted by our generalized formation scheme (Fig. 3). CH_2OHCHO is an efficient initiator in the prebiotic formation of sugars ([21]). HCN is a key molecule in the prebiotic synthesis of amino acids ([21], [22]) and nucleobases ([21]) and even offers an elegant pathway to sugars ([23]). $HCONH_2$ provides a prebiotic route to nucleobases ([24]). $HCONH_2$ ([24]) and CH_3CONH_2 ([21]) catalyze phosphorylation of nucleosides to nucleotides, in which amines also play a role ([21]). Isocyanates play a major role in the prebiotic synthesis of peptides, through the so-called isocyanate route ([22]). The complexity of cometary nucleus chemistry and the importance of N-containing organics imply that early solar system chemistry fosters the formation of prebiotic material in noticeable concentrations.

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SUPPLEMENTARY MATERIALS

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