Ammonium salts are a reservoir of nitrogen on a cometary nucleus and possibly on some asteroids

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INTRODUCTION: Comets and asteroids preserve information on the earliest stages of Solar System formation and on the composition of its building blocks. The nature of their solid material can be investigated by analyzing the sunlight scattered by their surfaces. The nucleus of comet 67P/Churyumov-Gerasimenko (hereafter 67P) was mapped by the Visible and Infrared Thermal Imaging Spectrometer, Mapping Channel (VIRTIS-M) on the Rosetta spacecraft from 2014 to 2015. The nucleus appeared almost spectrally uniform from 0.4 to 4 μm, characterized by a low reflectance of few percent, a reddish color, and an unidentified broad absorption feature around 3.2 μm, which was ubiquitous throughout the surface. The darkness and the color of comet 67P could be due to a mixture of refractory organic molecules and opaque minerals. Although water ice may contribute to the 3.2-μm absorption, it cannot explain the entire feature.

RATIONALE: Semivolatile compounds of low-molecular weight, such as carboxylic (−COOH)-bearing molecules or ammonium (NH₄⁺) ions, have been proposed as potential carriers of the 3.2-μm absorption feature. To test these hypotheses, we performed laboratory experiments to measure the reflectance spectra of these compounds mixed in a porous matrix of submicrometric opaque mineral grains, under simulated comet-like conditions (170 to 200 K, <10⁻⁵ mbar).

RESULTS: The 3.2-μm absorption feature is consistent with ammonium salts mixed with the dark cometary surface material. We attribute additional absorption features to carbonaceous compounds and traces of water ice. Several ammonium salts can match the absorption feature equally well: ammonium formate, ammonium sulfate, or ammonium citrate. A mixture of different ammonium salts could be present.

Ammonium salts at the surface of comet 67P could have been synthesized through acid-base reactions of ammonia (NH₃) with the corresponding acid molecules in solid ices. That reaction may have occurred in the interstellar medium, in the protoplanetary disk, or during the sublimation of the ices in the cometary nucleus.

The depth of the band suggests that the cometary surface contains an upper limit of ~40 weight % (wt %) of ammonium salts, but the exact concentration remains unknown. If the amount of ammonium salts is higher than ~5 wt %, they constitute the dominant reservoir of nitrogen in the comet, containing more nitrogen than the refractory organic matter and the volatile species, such as NH₃ and N₂. Consequently, the abundance of nitrogen in this comet is closer to that of the Sun than previously thought.

CONCLUSION: Ammonium salts may dominate the reservoir of nitrogen in comets. Their presence in cometary dust may explain increases of gas-phase NH₃ and HCN observed in some comets when close to the Sun, which could be caused by the thermal dissociation of ammonium salts. Several asteroids in the Main Belt, Jupiter’s Trojan asteroids, and its small moon Himalia have similar spectra to that of comet 67P, with a broad spectral absorption feature at 3.1 to 3.2 μm, which we suggest could also be due to ammonium salts. The dwarf planet Ceres has ammoniated phyllosilicates on its surface, which may have formed from ammonium ions inherited from outer Solar System objects with compositions similar to that of comet 67P. The presence of these salts on comet 67P, and possibly on other primitive Solar System bodies, suggests a compositional link between asteroids, comets, and the proto-solar nebula.

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Comparison of ammonium formate spectrum with the average spectrum of comet 67P. The average reflectance spectrum of comet 67P (black line) and the spectrum of a mixture of ammonium formate (NH₄⁺ HCOO⁻) with opaque grains measured in the laboratory under comet-like conditions (blue line). Also shown are views of the 4-km-diameter comet nucleus (Credit: ESA/Rosetta/NAVCAM–CC BY-SA IGO 3.0; http://creativecommons.org/licenses/by-sa/3.0/igo) and the 48-mm-diameter laboratory sample.
Ammonium salts are a reservoir of nitrogen on a cometary nucleus and possibly on some asteroids

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The measured nitrogen-to-carbon ratio in comets is lower than for the Sun, a discrepancy which could be alleviated if there is an unknown reservoir of nitrogen in comets. The nucleus of comet 67P/Churyumov-Gerasimenko exhibits an unidentified broad spectral reflectance feature around 3.2 micrometers, which is ubiquitous across its surface. On the basis of laboratory experiments, we attribute this absorption band to ammonium salts mixed with dust on the surface. The depth of the band indicates that semivolatile ammonium salts are a substantial reservoir of nitrogen in the comet, potentially dominating over refractory organic matter and more volatile species. Similar absorption features appear in the spectra of some asteroids, implying a compositional link between asteroids, comets, and the parent interstellar cloud.

The composition of comets and asteroids can be investigated from the light scattered by their surfaces. For objects of which the visible to near-infrared wavelength range shows no, or only weak, spectral features, analysis of the 3-μm region (between roughly 2.4 and 3.6 μm) can be used to investigate volatile and organic compounds present on their surfaces (1). The Visible and InfraRed Thermal Imaging Spectrometer, Mapping Channel (VIRTIS-M) instrument (2) on the Rosetta spacecraft observed the nucleus of comet 67P/Churyumov-Gerasimenko (hereafter 67P) in the spectral range of 0.2 to 5.1 μm (3). The surface imaged by VIRTIS-M appears almost spectrally uniform (4), characterized by a very low reflectance [geometric albedo of 6% at 0.55 μm (3)], positive (red) visible and infrared spectral slopes, and a broad absorption feature from 2.8 to 3.6 μm, centered at 3.2 μm (3, 4).

This absorption band, which has not been detected on other comets, is observed on all types of surface terrains and was persistently observed from August 2014 when comet 67P was 3.6 astronomical units (au) from the Sun and cometary activity was weak until just before the comet reached its closest point to the Sun and experienced maximum activity in May 2015 at 1.7 au, for as long as the VIRTIS-M infrared channel could record measurements (6). Analyses of the VIRTIS-M reflectance spectra ascribed the darkness and slope to a refractory polyaromatic carbonaceous component mixed with opaque minerals (anhydrous Fe-sulfides and Fe–Ni alloys), but the carrier of the 3.2-μm feature remained unknown (3).

Water ice contributes to this absorption on some parts of the surface (6–9), causing a broadening and deepening of the absorption feature from 2.7 to 3.1 μm, but cannot explain the entire feature (3, 10). Except in specific ice-rich areas, the surface of the cometary nucleus is uniform in composition, with a predominance of non-ice materials (9). Semivolatile materials of low molecular weight have been proposed as carriers of the 3.2-μm feature, with carboxyl (–COOH)–bearing molecules or NH₄⁺ ions being the most plausible candidates (11). How-
and/or differing properties of the salts present on the cometary surface (such as concentration, mixing, and counter-ions). We investigated other candidate compounds—fine water ice grains, carboxylic acid, or hydrated minerals—but these do not match the 3.2-μm feature (Fig. 1B). The laboratory spectra of five ammonium salts we investigated are shown in Fig. 2. Ammonium formate, ammonium sulfate, or ammonium citrate all reproduce the 3.1- and 3.3-μm absorption bands observed on the comet. For ammonium carbamate and ammonium chloride, the corresponding bands are shifted to longer wavelengths or have different spectral shapes (Fig. 2).

The similarity of band shapes and positions leads us to conclude that NH₄⁺ in ammonium salts is the main species responsible for the

Fig. 1. Comparison of NH₄⁺ HCOO⁻ spectrum with the average spectrum of comet 67P. (A) The average reflectance spectrum of comet 67P in the 3.0-μm region [(a), black line; the vertical scale is given in radiance factor I/F] and the spectrum of a sublimate residue containing ≤17 wt % ammonium formate mixed with ≥83 wt % pyrrhotite grains at 170 to 200 K [(b), red line; the vertical scale is given in reflectance factor REFF]. The same spectra overlain on each other is shown in fig. S5. Gaps in the comet 67P spectrum are due to the instrument’s diffraction order sorting filters. Both spectra have the same shape and minima at 3.1 and 3.3 μm (dashed gray vertical lines). (B) Reflectance spectra (normalized at 2.5 μm) of other compounds that do not match the comet 67P spectrum: (c) a model spectrum of 1-μm-diameter pure water ice grains (solid line) [Hapke model (60), using optical constants at 145 K (61), spectrum normalized, scaled by a factor of 0.14, and offset by –0.08]; (d) a measured spectrum of a sublimate residue containing ≤17 wt % lactic acid mixed with pyrrhotite grains at 170 to 200 K (dashed line, offset by –0.35) (12); and (e) spectrum of the primitive carbonaceous chondrite meteorite QUE 97990, which is rich in hydrous silicates, measured under 400 to 475 K and high vacuum (dotted line, offset by –0.55) (62). Between 2.5 and 2.8 μm, the spectra of sublimate residues are affected by measurement artifacts because of the presence of water vapor in the optical path. Residual spectra, calculated by dividing the comet 67P spectrum (a) by the experimental spectrum (b) or (d), are shown at the bottom of (A) and (B). Error bars indicate the ±1σ uncertainties.

Fig. 2. Reflectance spectra of several ammonium salts. Continuum-removed reflectance spectra of sublimate residues made of ammonium salts (colored lines) mixed with pyrrhotite grains (gray line) measured in high vacuum at 170 to 200 K, compared with the observed average spectrum of comet 67P (black line). Ammonium formate, citrate, and sulfate are the closest matches to the absorption features in comet 67P. We attribute the other absorption features in the comet spectrum at 3.35 to 3.6 μm to C–H stretching modes of organic compounds (10). Between 2.6 and 2.8 μm, the laboratory spectra are affected by measurement artifacts because of the presence of water vapor in the optical path. The mass fractions of the salts mixed with pyrrhotite are ≤9 wt % for ammonium sulfate and chloride, ≤17 wt % for ammonium formate and carbamate, and ≤23 wt % for ammonium citrate (the latter has been scaled by a factor of 0.6 for display). These spectra are shown in fig. S6 with uncertainties and before continuum removal.
3.2-μm feature. The counter-ion (in this case, the anion) is not fully constrained. The identification of HCOOH by the Rosetta Orbiter Spectrometer for Ion and Neutral Analysis (ROSINA) mass spectrometer (16) and the spectrum of ammonium formate (NH$_4^+$ HCOO$^-$) in Fig. 2 make it our favored candidate.

Origins of ammonium salts

There are several potential pathways for the synthesis of ammonium salts present at the surface of comet 67P. Ammonia (NH$_3$) has a high proton affinity, allowing it to transform easily into ammonium (NH$_4^+$), either in the gas (17) or in the solid phase. Ammonium and potential counter-ions (such as HCOO$^-$, CN$^-$, and OCN$^-$) may be produced by acid-base reactions of ammonia (NH$_3$) with the corresponding acids (such as HCOOH, HCN, and HNCO) or by nucleophilic addition of NH$_3$ with CO$_2$ or H$_2$CO, even at cryogenic temperatures in the solid phase (18, 19). These reactions have low activation energies and do not require an external source of photons, electrons, or cosmic rays (18). Some ions (such as OCN$^-$ and HCOO$^-$) can be produced at 10 to 14 K, but most of the ions we considered (such as NH$_2$COO$^-$ and CN$^-$) are produced at higher temperatures (19–21). Astronomical observations of interstellar ices have likely identified CN$^-$ (22–25) and possibly detected NH$_4^+$ (25–28). Ammonium salts can be formed upon sublimation of water ice containing NH$_3$ and counter ions (19, 20). It is possible that the NH$_4^+$ detected on comet 67P could be inherited from interstellar ices. In that case, the ammonium salts would be produced during further thermal processing of the ices, either in the protoplanetary disk (25) or during the sublimation of the ices in the cometary nucleus, through a process similar to the one simulated in our laboratory experiments. The production of ammonium salts by means of a gas phase reaction under astrophysical conditions has not been reported in the literature. Solid-state reactions appear more likely because proton transfer or nucleophilic addition are highly facilitated by a dust surface and a solvent such as ice (30, 31).

Comparison with other small bodies

The 3.2-μm absorption feature of comet 67P shares similarities with the 3-μm features observed on several asteroids, including the position and width of the band from 2.9 to 3.6 μm and the reflectance minimum at 3.1 to 3.2 μm (Fig. 3). However, the bands observed on most of these asteroids are distinct from the one of comet 67P, having a different shape and no secondary minimum at 3.3 μm (Fig. 3). Nevertheless, these spectra are compatible with the presence of ammonium salts, if the spectral differences are due to the environmental conditions at the surface of these small bodies (Fig. S7). The spectra of asteroids 24 Themis and 52 Europa are representative of objects found in the asteroid Main Belt (1, 32) and in orbit around Jupiter, such as the irregular moon Himalia (33). The dwarf planet 1 Ceres has ammonium-bearing minerals on its surface, with absorption features at 2.72 and 3.06 μm (Fig. 3), mostly in the form of phyllosilicates but with smaller amounts of salts (34). Our identification of ammoniated salts on a comet supports the hypothesis that materials on Ceres may have originated from the outer Solar System (34).

Volatility of ammonium salts

There is weak evidence for ammonium salts in meteorites, micrometeorites, and interplanetary dust particles (IDPs) (35, 36). Because these salts are more volatile than most refractory material, they might not be preserved during atmospheric entry of small particles and/or during long periods of time under terrestrial environmental conditions (35). Ammonium salts contained in grains ejected from cometary nuclei may react and/or sublimate when heated by the Sun and act as distributed sources of gases in comae, the envelopes of gas and dust around cometary nuclei (37). This could explain observed increases of NH$_3$ and HCN when some comets reach short heliocentric distances (<1 au from the Sun), such as comet C/2012 S1 (ISON), which experienced multiple outbursts as it disrupted inside ~0.8 au (38, 39). On comet 67P, the decomposition of ammonium formate (NH$_4^+$ HCOO$^-$) could produce formamide (NH$_2$CHO), which has been detected by the ROSINA instrument.

**Fig. 3.** The spectrum of comet 67P compared with other Solar System bodies. Reflectance spectra normalized at 2.9 μm are of comet 67P (offset by +0.45); the Main Belt asteroids 24 Themis (offset by +0.31) (63), 65 Cybele (offset by +0.19) (64), 52 Europa (32), and 361 Bononia (offset by +0.07) (32); the average spectrum of six Jupiter Trojan asteroids [(65), their “less red” group] (divided by 3 and offset by +0.49); and the average spectrum of 1 Ceres (scaled by a factor of 0.5, and offset by +0.19) (34). The spectrum of Jupiter’s irregular moon Himalia is almost indistinguishable from 52 Europa (33). For each spectrum, the dots are the observational data (plotted directly for Europa and Bononia, digitized from the literature for the other objects), and the solid lines are running average spectra. The blue dashed line shows the averaged extrapolation of the six Jupiter Trojan’s $K$-band spectra (66). The gray dashed line shows the position of the band at 3.11 μm on comet 67P spectrum. The red and green vertical marks indicate the positions of the maxima of absorption of ammonium formate and ammonium chloride respectively, shown in Fig. 2.

Absorption features around 3.1 to 3.2 μm on some of these bodies are similar to the ammonium salt features on comet 67P. Ceres exhibits different features, which are due to ammoniated phyllosilicates (34).
and is compatible with the mass spectrum measured by the Cometary Sampling and Composition (COSAC) experiment on Rosetta’s Philae lander (40–42). The volatility of an ammonium salt strongly depends on the anion; for example, at a pressure of 1 atm, ammonium formate decays at 389 K, ammonium sulfate at 553 K, and ammonium chloride at 611 K (43). Under simulated astrophysical conditions (10–6 mbar), the sublimation temperatures of ammonium salts are 160 to 180 K for ammonium cyanide (NH4+ CN−) (44), 200 to 230 K for ammonium formate (NH4+ HCOO−) (30, 45), and 230 to 260 K for ammonium carbamate (NH4+ NH2COO−) (46). Because of these differences of volatility, the composition of ammonium salts observed on comet or asteroid surfaces, and the gases produced by their decomposition, may change with the heliocentric distance.

**Nitrogen budget of comet 67P**

Rosetta’s Cometary Secondary Ion Mass Analyzer (COSIMA) collected coma dust grains 10 to 30 km from comet 67P’s nucleus and measured their composition (47). Ammoniated salts were not detected, possibly because any semivolatile compounds present in the dust grains would have sublimated during the multiple-day-long pre-analysis storage of the particles at 283 K (47). If ammonium salts had been lost from the dust grains analyzed by COSIMA, their measured nitrogen-to-carbon ratio (N/C) would be a lower limit, missing the contribution of the semivolatile nitrogen-bearing salts. COSIMA measured an average N/C of 0.035 ± 0.011, which is similar to the ratio found in the insoluble organic matter extracted from carbonaceous chondrite meteorites and in most micrometeorites and interplanetary dust particles (47) but lower than the solar N/C value of 0.29 ± 0.12 (48). Similar depletions in nitrogen compared with the Sun have been found in the refractory dust and gas phases of other comets (49–51).

We propose that ammonium salts may constitute a substantial nitrogen reservoir in comet 67P and possibly other comets and small bodies. The 3.2-μm band observed in the spectrum of comet 67P is 5 to 20% less deep than the band of ammonium formate in our sublimates residues (fig. S6) (12). Assuming that the physical parameters that control the light scattering (such as mixing modes and grain sizes) of the sublimates residues are similar to that of the cometary surface, we derived an upper limit of the volumetric abundance of salts in the dark surface material of the comet of ~40 vol %. The dark surface material is a mixture of ~45 wt % organic (~1 g/cm³) and ~55 wt % mineral (~3.4 g/cm³) components, estimated from COSIMA measurements (52).

Taking into account this composition, we derived an upper limit of the mass fraction of ammonium salts mixed with the dust of ~40 wt %, but we cannot determine the surface abundance of ammonium salts on the comet exactly (12). If the mass fraction of ammonium formate (NH4+ HCOO−) is 5 wt % in the cometary dust, the total atomic nitrogen in the comet is distributed as ~47% N in ammonium salts, ~52% N in refractory organic matter, and ~1% N in volatiles (Fig. 4); the whole comet would then have a N/C ratio of about 0.06 (Fig. 5). If there is a mixture of
several ammonium salts, then NH₄⁺ would have a range of counter-ions, some of them N-bearing, which would raise the N/C ratio. Shown in Fig. 3 is how the inferred N/C ratio of the comet increases with the assumed concentration of ammonium salts in the dust and depends on the nature of the counter-ions of NH₄⁺.

**Implications**

The identification of ammonium salts on comet 67P shows that this comet, and possibly others, could have a N/C ratio higher than previously thought. If ammonium salts are a substantial repository of nitrogen, assessment of their ¹⁴N/¹⁵N isotopic ratio and comparing it with the proto-solar ratio could inform models of the incorporation and evolution of nitrogen in the early Solar System (53). If ammonium salts were also present in sufficient abundance in planetesimals during the early Solar System, they would have provided a solid form of nitrogen closer to the Sun than N₂ and NH₃ ices and therefore available for planetary accretion (54). Abundant ammonium salts would have lowered the melting point of water ice in the subsurface of icy bodies (55). When mixed in liquid water, ammonium salts are known to participate in potentially biotic reactions, such as the formation of pyrimidine and purine nucleobases (56), the production of amino acids (57), the phosphorylation of nucleoacides (58), or the formation of dye molecules (59).

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Competing interests: We declare no competing interests.

Data and materials availability: The laboratory reflectance spectra are available in the Grenoble Astrophysics and Planetology Solid Spectroscopy and Thermodynamics (GnoST) database (67, 68). The average reflectance spectrum of comet 67P measured by VIRTS is available from (60), their ‘source data Fig. 1.’ The reference spectra of Mars and Lutetia are available from the Planetary Science Archive (https://archives.esac.esa.int/psa/wftable%20view by selecting Mars or 21 Lutetia as the target, VIRTS (Rosetta) as the instrument, clicking search, then filtering by observation Ids 11_00130974021 for Mars or 11_00237396952 for Lutetia.

SUPPLEMENTARY MATERIALS

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Materials and Methods

Figs. S1 to S9
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Ammonium salts on comet 67P

The distribution of carbon and nitrogen in the Solar System is thought to reflect the stability of carbon- and nitrogen-bearing molecules when exposed to the heat of the forming Sun. Comets have a low nitrogen-to-carbon ratio, which is contrary to expectations because they originate in the outer Solar System where nitrogen species should be common. Poch et al. used laboratory experiments to simulate cometary surfaces and compared the resulting spectra with comet 67P/Churyumov-Gerasimenko. They assigned a previously unidentified infrared absorption band to nitrogen-containing ammonium salts. The salts could contain enough nitrogen to bring the comet's nitrogen-to-carbon ratio in line with the Sun's.

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