

Elements

An International Magazine of Mineralogy, Geochemistry, and Petrology

Provided for non-commercial research and education use.
Not for reproduction, distribution or commercial use.



This article was published in *Elements –An International Magazine of Mineralogy, Geochemistry, and Petrology*. The attached copy is provided to the authors for non-commercial research and education use. It can be used for instruction at the author's institution, shared with colleagues, and provided to institution administration.

Other uses, including reproduction and distribution or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

www.elementsmagazine.org
www.elements.geoscienceworld.org

Organic Molecules and Volatiles in Comets

CREDIT: ESA/OSIRIS

Hikaru Yabuta¹, Scott A. Sandford² and Karen J. Meech³

1811-5209/18/0014-0101\$2.50 DOI: 10.2138/gselements.14.2.101

Organic molecules and volatiles (e.g. H₂O, CO, CO₂) are the major components of comets. The majority of the organic compounds found within comets were produced by ice irradiation in dense molecular clouds and in the protoplanetary disk prior to comet formation. Comets are essentially repositories of protocometary material. As a result, comets do not show the clear trends in chemical and isotopic compositions that would be expected from our understanding of their formation locations. Rather, comets record chemical evolution in the protoplanetary disk and allow us to unveil the formation history of the organics and volatiles.

KEYWORDS: organic molecules, water, carbon monoxide, carbon dioxide, sublimation processes, volatiles.

INTRODUCTION

Organic molecules and volatiles (e.g. H₂O, CO, CO₂) are major building blocks of planets, as evidenced by the fact that their constituents (H, C, O, N, and S) are among the most abundant elements in the solar system. The first organic molecules and volatiles were produced in interstellar clouds through photochemical reactions in the gas phase and on dust surfaces. These first molecules were then involved in further decomposition and synthesis reactions through thermal, photochemical, and aqueous processes in the protoplanetary disk and within planetesimals (the precursor bodies to larger planets). The variety of processes and locations for molecular formation resulted in the observed diversity in the chemical composition of asteroids and comets.

During the first few million years of solar system history, when gas was present in the protoplanetary disk, ices condensed out of the nebular gases far from the Sun and were incorporated into planetesimals, imparting a local chemical signature. Thus, cometary organics and volatiles record the chemical evolution of the protoplanetary disk and preserve the link between interstellar clouds and planetesimals. Although asteroids have been regarded as the most likely source of water to the terrestrial planets (Altwegg et al. 2015), comets must also have contributed to the inventory of volatiles (Marty et al. 2017).

Mixed molecular ices are a major component of cometary nuclei, which is not surprising given that such ices are abundant in dense interstellar molecular clouds and protoplanetary disks, the precursor environments in which comets form. The main constituents of these ices are H₂O, CO and CO₂, but many other molecular species are present, including methanol (CH₃OH), methane (CH₄), ammonia (NH₃), formaldehyde (HCHO), acetylene (C₂H₂), ethane (C₂H₆), hydrogen cyanide (HCN), and hydrogen sulfide (H₂S). A

comet warms as it approaches the Sun and volatiles sublimate, causing escaping gas to carry away solids, which produces the cometary coma (the atmosphere of a comet) and that distinctive gas and dust tail we sometimes get to see from Earth.

Another major component of cometary nuclei is refractory (i.e. heat resistant) organic material. The distribution and composition of this material are revealed through direct sample analysis combined with remote sensing observations. The cometary refractory organics are usually compared with organic materials detected in primitive carbonaceous chondrite meteorites. Historically, interplanetary dust particles and Antarctic micrometeorites included the first cometary materials available for laboratory analysis (see “Cosmic Dust” issue of *Elements*, June 2016), but it has been impossible to distinguish cometary dust from asteroidal dust. A turning point in the expansion of analytical techniques in organic cosmochemistry came when NASA’s *Stardust* mission to comet Wild 2 returned cometary dust particles to Earth: special techniques were developed with high spatial resolutions and/or high sensitivities. The submicron-size heterogeneities of the molecular and isotopic compositions in these samples disclosed the precursor compounds and formation pathways of the refractory organic materials in the early solar nebula. They potentially permit subdivision of the most primitive (never heated) comets and asteroids into several evolutionary stages. In this article, we review cometary organic and volatile compounds revealed through observations, experiments, sample analyses, and spacecraft missions.

GROUND-BASED AND FLYBY OBSERVATIONS

One of the goals of assessing the comet volatile inventory has been to understand to what extent the materials in comets have been processed during formation or if they represent pristine material inherited from the interstellar medium. Ideally, one would like to trace the most abundant

¹ Department of Earth and Planetary Systems Science
Hiroshima University
Kagamiyama 1-3-1 Hiroshima 739-8526, Japan
E-mail: hyabuta@hiroshima-u.ac.jp

² NASA Ames Research Center
Moffett Field, CA 94035, USA
E-mail: Scott.A.Sandford@nasa.gov

³ Institute for Astronomy, University of Hawaii
2680 Woodlawn Drive
Honolulu, HI 96822, USA
E-mail: meech@ifa.hawaii.edu

molecular species that are also seen in molecular clouds. The chemistry of comets was first studied from Earth, starting with the advent of optical wavelength spectroscopy during the late 1800s. Since then, this exploration has expanded to include studies done at ultraviolet (UV), infrared (IR) and radio wavelengths, and through in situ mass spectrometry during the European Space Agency's *Rosetta* mission to comet 67P/Churyumov–Gerasimenko (Meech 2017).

Molecular species that sublimate directly from a comet's nucleus are called “parent molecules” and their photodissociation products are called “daughter species”. Most of the species observed at optical wavelengths do not represent the parent molecules but, instead, are produced in the coma through photolysis or chemical reactions. Three decades of spectroscopy through two large surveys has shown that comets have remarkably similar compositions, varying little with distance from the Sun. However, comets seem to fall into two distinct chemical groups, one group being depleted in carbon-chain species, namely in the carbon radicals C_2 and C_3 (A'Hearn et al. 1995). Such depleted comets are primarily short-period Jupiter-family comets, likely formed at Kuiper Belt distances, although some long-period comets are also depleted in C_2 and C_3 radicals (FIG. 1A). This has been interpreted as resulting from temperature-related chemical effects in the protoplanetary disk associated with the comets' formation environment, but is not yet well understood.

To date, several dozen parent molecules have been identified, and their abundances computed with respect to water (e.g. Mumma and Charnley 2011). The parent molecule CO has now been routinely measured in the UV from the Hubble Space Telescope. However, most of the ground-based information about parent molecules has come from observations in the near-IR and at radio wavelengths. The relative abundance of the parent molecules vary by about a factor of 10 between comets. Often this is compared with abundances relative to water in the interstellar medium, but these comparisons need to be taken with caution. Direct observation of H_2O (which must be done in the IR) is often not done; therefore, the abundance is inferred either from non-simultaneous optical detection of the photodissociation product OH in the UV or at radio wavelengths, from which determining a water production rate requires sophisticated modeling. More recently, high-resolution near-IR spectroscopy on large telescopes has enabled the

detection of many parent molecules simultaneously with water (Mumma and Charnley 2011). A pattern in composition is emerging that is similar to that seen in the carbon-chain molecules at optical wavelengths: there are some comets that are volatile organic rich, normal, and depleted (FIG. 1B).

Carbon dioxide cannot be directly observed from the ground because of strong absorption by terrestrial CO_2 . Direct information about this important and abundant molecule comes from space observations. Carbon dioxide was first detected in a comet in 1986 by the European Space Agency's *Giotto* mission to comet 1P/Halley. Subsequently, NASA's infrared Spitzer Space Telescope, the Japan Aerospace Exploration Agency's *Akari* infrared satellite, and NASA's *WISE* (wide-field infrared explorer) satellite have all provided significant information about CO_2 abundance in comets. The abundance of CO_2 relative to H_2O varies significantly between both long-period comets and short-period comets (FIG. 1C). Within 3 astronomical units (one astronomical unit being the average distance between the Sun and Earth), which is where water strongly sublimates and a meaningful assessment of relative abundance can be made, the abundances of CO_2 range from a few percent up to 30% relative to water (Ootsubo et al. 2012). As with other volatiles, there is no particular trend in abundance with comet formation location (e.g. Jupiter-family comets versus long-period comets); however, all the strongly CO_2 -depleted comets seen to date are Jupiter-family comets.

Space missions have provided key insights into the three primary volatiles (H_2O , CO, CO_2) most easily linked to the Earth-based protoplanetary disk observations made at the international ALMA (Atacama Large Millimeter/submillimeter Array) facility in Chile. The NASA *Deep Impact* mission to comet 9P/Tempel 1 showed that the water-ice that was driving the comet's activity was close to the surface, whereas CO_2 gas, which emanated from the night-side and was the likely driver of jets, probably originated within a depth that solar heat was able to penetrate in one orbit, i.e. ~1 m depth. Both H_2O and CO_2 had very different distributions around the nucleus (A'Hearn et al. 2008), suggesting that the nucleus was made of smaller planetesimals with different compositions. Data from the *EPOXI* mission [A NASA mission that combined two ongoing Discovery Program missions, including the *Deep Impact* spacecraft] showed this even more dramatically (FIG. 2A). It was clear that CO_2 , not H_2O , was the main driver of activity

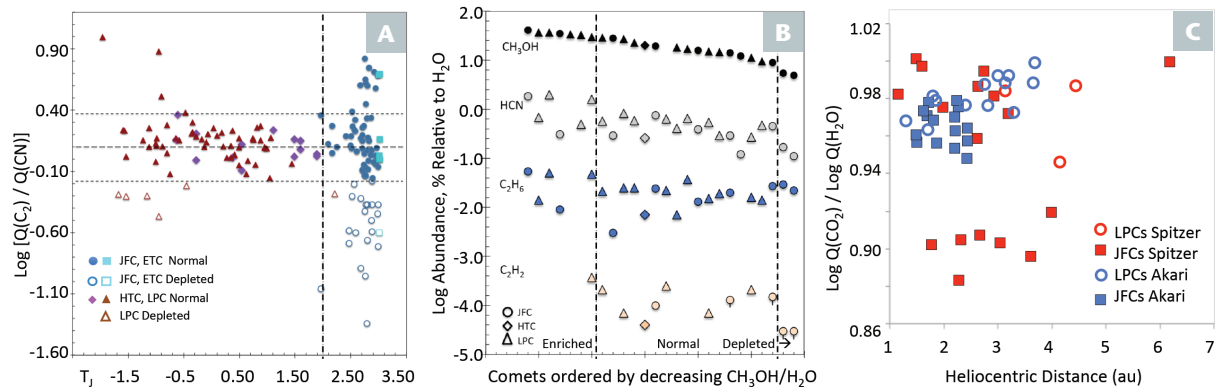


FIGURE 1 (A) Plot of the ratio of C_2/CN abundance determined through optical spectroscopy versus the Tisserand invariant, T_j , a proxy for orbital dynamical class. This illustrates that some comets are depleted in carbon-chain species (Meech et al. 2017). Abbreviations: JFC = Jupiter-family comet, ETC = Encke-type comet, HTC = Halley-type comet, LPC = long-period comet. (B) Abundances of volatile organic species obtained at near-IR wavelengths. As in the case of the carbon-chain compounds in

FIGURE 1A, some comets are enriched, normal, and depleted (delineated by the vertical lines) in parent organic volatiles (CH_3OH , HCN, C_2H_6 , C_2H_2). DATA FROM MUMMA AND CHARNLEY (2011) AND DELLO RUSSO ET AL. (2016). (C) Abundance of CO_2 relative to water for Jupiter-family comets and long-period comets from the near-IR space surveys conducted by the Spitzer satellite (red symbols) and Akari satellite (blue symbols). There is no strong trend in CO_2 abundance with heliocentric distance (Meech et al. 2017).

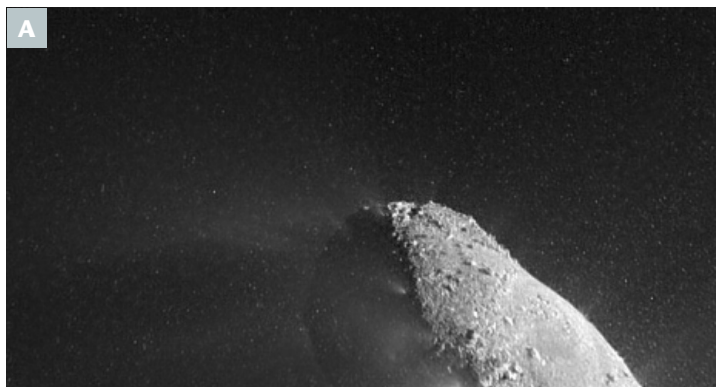
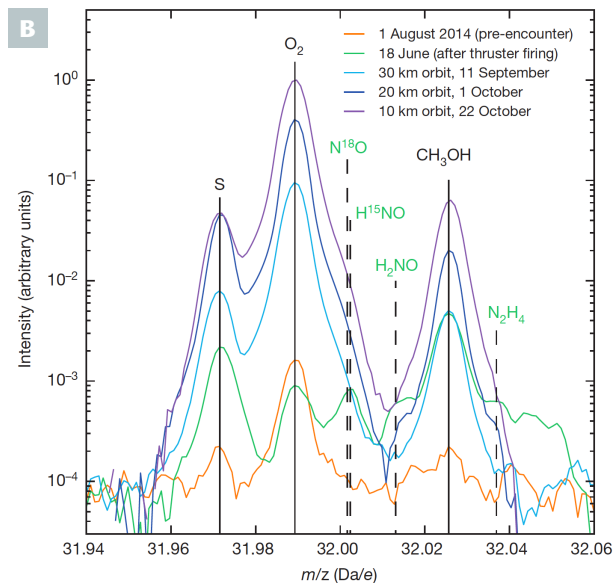


FIGURE 2 (A) Closeup of comet 103P/Hartley 2 (~1.6 km in diameter) from the *EPOXI* mission, showing the night-side jet activity driven by subsurface CO₂ sublimation. CREDIT: NASA/JPL-CALTECH/UMD. (B) Mass spectrum (mass-to-charge ratio, m/z) from the coma of 67P/Churyumov–Gerasimenko showing the strong detection of molecular oxygen obtained during 2014 by the *Rosetta* Orbiter Spectrometer for Ion and Neutral Analysis (ROSINA) instrument. Other notable peaks are sulfur (S) and ethanol (CH₃OH). AFTER BIELER ET AL. (2015).



in comet 103P/Hartley 2 near perihelion (closest approach to the Sun), and this CO₂ was likely coming from a subsurface source (A’Hearn et al. 2011). The *Rosetta* mission also observed strong dichotomies in the relative ratios of CO₂/H₂O between the northern and southern hemispheres of comet 67P/Churyumov–Gerasimenko, as well as changing mixing ratios of less abundant molecules, as seen from in situ near-IR measurements (Hässig et al. 2015). However, much of the change in cometary CO₂/H₂O ratio has been attributed to seasonal effects. As sunlight reaches new parts of a comet’s surface, older layers are removed and dust from the southern hemisphere is redeposited in the north.

LABORATORY EXPERIMENTS ON COMETARY AND PRECOMETARY ICE ANALOGS

Sublimation processes in mixed-molecular ices [ices containing mixtures of different molecular species] can be quite complex. Simple ices made of a single type of molecule, for example H₂O, sublime at well-defined rates over specific temperature ranges, that can be characterized in the laboratory. However, mixed-molecular ices can produce more complex behaviors. Because H₂O forms ices with strong hydrogen bonds, its sublimation behavior often controls the release of less abundant, more volatile, molecular species trapped within the H₂O ice matrix. For example, CO trapped at low concentrations in warming H₂O-rich ices is not released near 30 K, which is where pure CO ice sublimates. Instead, CO is partially released when the H₂O ice structure undergoes higher-temperature phase changes upon warming, and the final CO is only lost when the H₂O ice matrix itself evaporates near 150 K (Sandford and Allamandola 1988). Ices that are H₂O-rich and that contain CH₃OH (methanol) can display even more complex behavior: such ices can spontaneously form Type II clathrate structures when warmed through 125 K in a vacuum. This process can lead to selective expulsion of excessive CH₃OH and other molecules like CO and CO₂ that cannot be accommodated by the clathrate structure (Blake et al. 1991). As a result, comets show a range of activity levels and activity rates as they approach the Sun.

In addition to driving cometary activity, mixed-molecular ices may play a large role in the chemical production of more complex organic compounds. Interstellar clouds and protoplanetary disks are both excellent sites for astrochemistry, in large part because they contain regions with very

low temperatures ($T < 50$ K). At these low temperatures, most molecules and many atoms will freeze and form icy mantles on dust grains, allowing them to interact in ways not possible when they are widely dispersed in the gas phase. Although traditional equilibrium chemistry cannot proceed to any significant extent, the presence of ionizing radiation in the form of high-energy photons or cosmic rays can drive reactions through the creation of ions and radicals that have no energy barriers when reacting with neighboring molecules. The result is a “chemistry of convenience” that has more to do with nearest neighbors than equilibrium or redox considerations (Sandford et al. 2015).

However, ice irradiation is not likely to greatly alter overall compositions of comets after they form because even energetic cosmic rays can only penetrate the surface layers of comets. Within the bulk of the comet, ice irradiation can only occur as a consequence of the decay of embedded radionuclides. Thus, the majority of organics in comets were produced by ice irradiation and were likely produced prior to cometary formation during earlier ice exposure in dense molecular clouds and in the protoplanetary disk (Ciesla and Sandford 2012). In this respect, comets are more repositories than factories.

Laboratory studies of the irradiation and warming of mixed ices of astrophysical interest over the past 25+ years have demonstrated that the exposure of ices to ionizing radiation leads to a rich chemistry that produces an wide variety of complex organic compounds, many of which remain unidentified (Fig. 3). However, amongst the products are numerous molecules of astrobiological interest—amino acids, amphiphiles, sugars, nucleobases (Fig. 4), and quinones (see Sandford et al. 2015 and references therein). This means that comets are potential repositories for many materials that could have played significant astrobiological roles. This is one of the reasons that comets may have played a key role in providing the early Earth with the critical materials needed to start life. The laboratory experiments described above and the detection of organic molecules in cometary comae (see discussion below) give some credence to this idea.

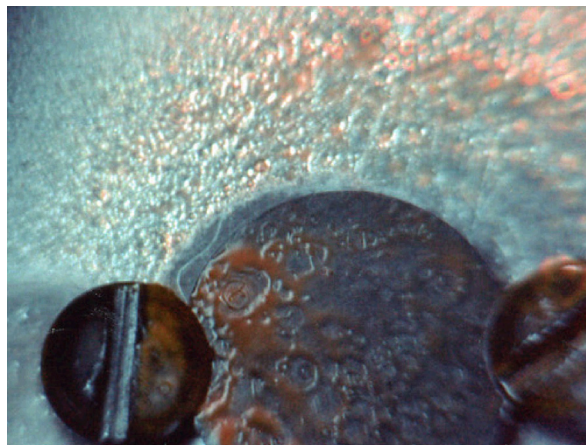
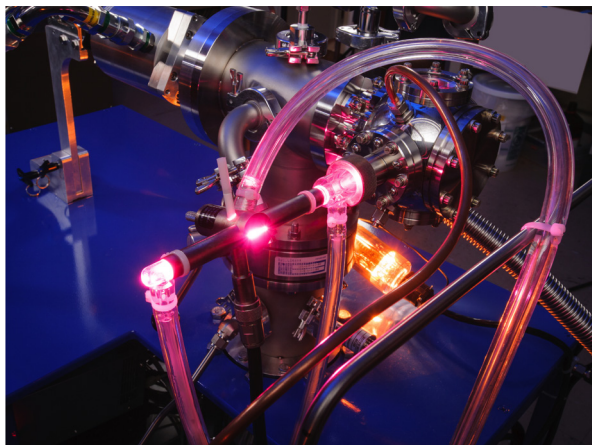


FIGURE 3 (LEFT) Laboratory simulations can use a cryovacuum system to demonstrate that the irradiation of ices of astrophysical composition can result in the production of complex organic residues. (RIGHT) The reddish-brown patches are the complex organic residues that remain on a 1 cm circular copper

sample holder mounted on an aluminum cold finger after an astro-physical ice analog is irradiated and warmed to remove the remaining original ice components. These residues contain many molecules of astrobiological interest such as amino acids, amphiphiles, and sugars.

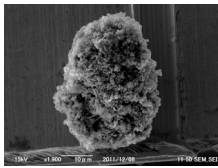
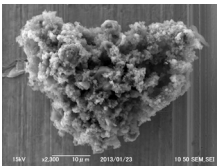
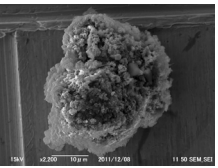
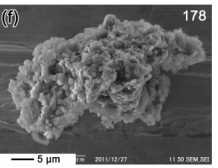
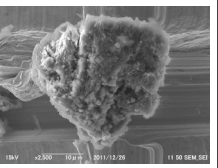
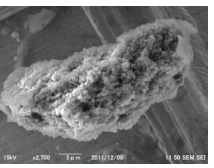
SAMPLE ANALYSES OF ORGANICS IN DUST PARTICLES DERIVED FROM COMETS

Chondritic porous interplanetary dust particles are the most primitive materials in the solar system. They are thought to be derived from short-period comets and contain higher carbon contents (>12%) than those of primitive carbonaceous chondrites (2%–5%). Isotopic compositions of interplanetary dust particles vary between and within individual particles: hydrogen isotopic compositions (δD) range from -420‰ to $24,800\text{‰}$, and nitrogen isotopic compositions ($\delta^{15}N$) range from -93‰ to 480‰ (Messenger 2000). Enrichments of D and ^{15}N are explained by isotopic fractionation reactions in extremely cold environments, such as interstellar clouds or the outer solar nebula. Enrichments of D and ^{15}N are also found in insoluble organic matter in primitive carbonaceous chondrites

(Busemann et al. 2006), indicating that the precursors of organic materials found in interplanetary dust particles and carbonaceous chondrites may have a common origin.

Organic materials in some of the dust particles collected by the *Stardust* spacecraft from comet 81P/Wild 2 are poor in aromatic carbon. These dust particles are, however, enriched in aliphatic carbon, and compounds containing nitrogen- and/or oxygen-bearing functional groups, such as nitriles, amides, carboxyls and alcohols (Sandford et al. 2006; Cody et al. 2008). These molecular features are distinct from the insoluble organic matter from primitive carbonaceous chondrites. Other dust particles from comet 81P/Wild 2 have a similar organic functional group chemistry to chondritic insoluble organic matter, and some of the organic nanoglobules found in *Stardust* samples are highly aromatic (De Gregorio et al. 2011). This diversity

TABLE 1 Characteristic features of minerals and organic materials in micrometeorites investigated in Noguchi et al. (2017). Samples D10IB004, D10IB356, D10IB004, D10IB178, D10IB163, and D10IB017 are all micrometeorites found from the surface snow near Dome Fuji Station in Antarctica. Abbreviations: MM = micrometeorite; CP MM = chondritic porous micrometeorite; GEMS = glass with embedded metal and sulfides; IOM = insoluble organic matter.

Sample ID	CP MMs (anhydrous)			Fluffy fine grained MMs (hydrous)		
	D10IB009	D10IB356	D10IB004	D10IB178	D10IB163	D10IB017
						
Mineralogy	GEMS, Metal, Sulfide, Olivine, Low-Ca pyroxene	GEMS, Metal, Sulfide, Olivine, Low-Ca pyroxene	GEMS, Metal, Sulfide, Olivine, Low-Ca pyroxene	Amorphous silicate, Olivine, Low-Ca pyroxene, Fe-rich saponite, Minor Fe-rich serpentine	Olivine, Low-Ca pyroxene, Fe-rich saponite, Minor Fe-rich serpentine	Olivine, Low-Ca pyroxene, Fe-rich saponite, Minor Mg-rich serpentine, Magnesite
Organic chemistry	Carboxyls (COOH), Aliphatic, Nitrile (CN) or N-heterocycles Abundant globules	COOH, Aliphatic	Aromatic, Aromatic ketone, COOH Chondritic IOM-like	–	Aromatic, Aromatic ketone, COOH Chondritic IOM-like One globule	Aromatic, Aromatic ketone, COOH Chondritic IOM-like
Isotope	$\delta^{15}N = \sim 600\text{‰} - 1,000\text{‰}$ $\delta D = \sim 8,000\text{‰} - 1,0000\text{‰}$	–	$\delta^{15}N = \sim 300\text{‰}$ $\delta D = \text{normal}$	–	–	–
Aqueous alteration	No	No	No	Weak	Weak	Moderate

in organic molecular compositions suggest that 81P/Wild 2 was not equilibrated and contains organic materials not found in meteorites or their asteroid parent bodies.

Polycyclic aromatic hydrocarbons ranging from 1-ring to 6-rings are seen in both comet 81P/Wild 2 dust particles and carbonaceous chondrites (Sandford et al. 2006). Methylamine, ethylamine, and glycine detected from the comet-exposed aerogel capture media are thought to be the products from energetically processed ice grains containing NH_3 , CH_4 , and C_2H_6 (Glavin et al. 2008). Detection of only one amino acid from comet 81P/Wild 2 is in significant contrast to the detection of >70 kinds of amino acids from carbonaceous chondrites, although this is probably largely due to the fact that *Stardust* samples are so small that the amino acid abundances are below current detection limits. Another possible reason is that the formation of amino acids did not occur efficiently in cometary icy bodies, because the many reactions that are needed to form amino acids require liquid water (e.g. Strecker synthesis). Nevertheless, some amino acids can, in fact, be made by direct ice irradiation.

Recent study of Antarctic micrometeorites has revealed wide variations in mineralogy and organic materials, reflecting differences in the extent of aqueous alteration on cometary and/or icy asteroidal bodies. Despite the similar mineralogy, the organic chemistry of the chondritic porous micrometeorites shows considerable diversity (Noguchi et al. 2017) (TABLE 1). Organic materials enriched in carboxyl groups ($-\text{COOH}$) and/or nitrogen-heterocycles that probably preserve the precursor compositions formed in interstellar cloud or the outer solar nebula. The organic materials would have been hydrolyzed during the early stages of aqueous alteration, which is a weaker degree of aqueous alteration than those of most carbonaceous chondritic parent bodies. Furthermore, they would have been converted to highly aromatic compositions similar to insoluble organic matter in primitive carbonaceous chondrites. The variations in molecular and isotopic compositions of organic materials in the Antarctic micrometeorites suggest that their organic precursors, original formation locations, and formation pathways of organic materials likely differed between the cometary parent bodies.

Ultracarbonaceous Antarctic micrometeorites (UCAMMs) are a rare type of micrometeorite that commonly contain large amounts of organic material enriched in nitrogen-bearing functional groups (e.g. nitrogen-heterocyclics, nitriles, and others) (Fig. 5). A high abundance of amorphous silicate grains and GEMS (glass with embedded metals and sulfides) are also characteristic of UCAMMs. As is the case for stratospheric interplanetary dust particles, UCAMMs show a wide range of H isotopic compositions (Duprat et al. 2010; Yabuta et al. 2017). Duprat et al. (2010) suggested that the organic materials in UCAMMs could have been produced in the outer protoplanetary disk. Yabuta et al. (2017) found evidence for a very weak degree of aqueous alteration of a UCAMM and suggested that the abundant organic material of UCAMMs was formed by a very small amount of fluid acting over a short duration, possibly from impact shock.

ROSETTA'S ANALYSIS OF COMET 67P/CHURYUMOV-GERASIMENKO

The *Rosetta* mission was the first mission to rendezvous with Jupiter-family comet 67P/Churyumov-Gerasimenko. Not only did it make remote observations, it also sent a small craft (*Philae*) to land on its surface and make in situ analyses of organics and volatiles. The *Rosetta* mass spectrometer detected about 60 volatile species in the coma of the comet. Although *Rosetta* could not measure

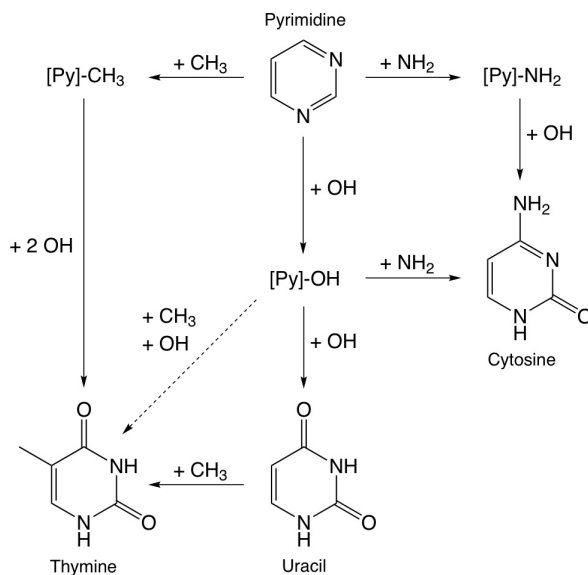


FIGURE 4 The routes by which three of the nucleobases—thymine (T) at bottom left; uracil (U) at bottom center; and cytosine (C) at right center—can be formed by the irradiation of an ice containing the *N*-heterocycle pyrimidine “[Py]” (top center).

global abundances, it did observe differences between the hemispheres, possibly reflecting evolutionary differences.

The visible, infrared, and thermal imaging spectrometer (VIRTIS) showed that water is largely absent from the surface of 67P/Churyumov-Gerasimenko, except for small spots of water-ice indicating that the surface is dehydrated by solar heating (e.g. Quirico et al. 2016). For the first time, dark refractory organic materials, which may be associated with opaque minerals (e.g. Fe-Ni metals and FeS), were discovered on a comet's surface. Its reflectance spectra with low albedo features are distinct from those of insoluble organic matter in carbonaceous chondrites, but are close to the aliphatic- and carboxyl-rich organic materials produced by UV irradiation of cometary ice analogs (Quirico et al. 2016).

In addition, the *Rosetta* orbiter's mass spectrometer for ion and neutral analysis (ROSINA) detected abundant CO_2 and ethane relative to water from the coma of 67P/Churyumov-Gerasimenko (Le Roy et al. 2015). Also of note is the detection of abundant molecular oxygen at the 4%

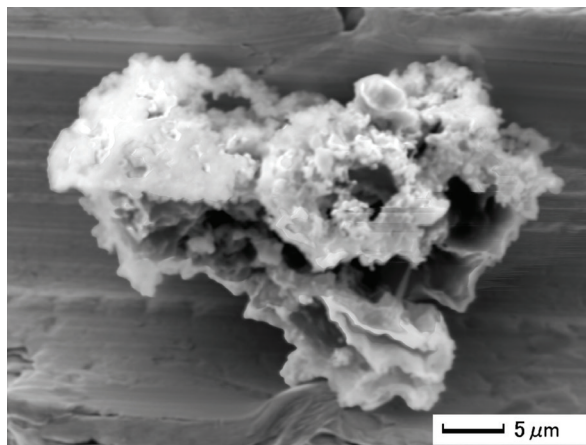


FIGURE 5 Ultracarbonaceous micrometeorite (D05IB80) collected from the surface snow near Dome Fuji Station, Antarctica (Yabuta et al. 2017). Scale bar = 5 μm.

level (Fig. 1C). Because protoplanetary disk models suggest that O₂ can only form in the gas phase at mid layers, and because of the strong correlation of O₂ with H₂O, it has been suggested that the O₂ is preserved from the interstellar medium (Bieler et al. 2015).

It had been expected that the sources of volatile inventory to the terrestrial planets were recorded in the hydrogen isotopic compositions of small bodies. ROSINA revealed that the D/H ratio of water from 67P/Churyumov–Gerasimenko [(5.3 ± 0.7) × 10⁻⁴] was approximately three times the terrestrial value (Altwegg et al. 2015). If comet 67P/Churyumov–Gerasimenko is representative of all comets, then it is unlikely that comets are the major source of Earth's water. However, given the large variation in D/H seen in comets so far, no firm conclusion can yet be drawn. An asteroidal origin for terrestrial water is more likely, based on the similarity in D/H between carbonaceous chondrites and terrestrial ocean water.

IMPLICATIONS OF COMETARY DATA TO THE FORMATION OF THE SOLAR SYSTEM

(1) Small primitive bodies witnessed the solar system's formation. During the first few million years of the solar system, a local chemical signature was imprinted on these planetesimals. Models of the chemistry of the early disk employ chemical networks of hundreds of gas-phase and grain-species reactions and can also be coupled with hydrodynamic models. The chemical products predicted by these models show complex molecular distributions both radially and vertically. The connection to today's solar system and the delivery of organics and volatiles to planets in the habitable zone relies on how this early material was dynamically redistributed during planet formation. There

are numerous dynamical models that can explain many of the features of our solar system, but these models differ on where these source material actually originated and how any of it reached the inner solar system. This makes the interpretation of volatile data from comets challenging.

(2) The presence in comets of intimate associations of volatiles, organics, and minerals that are not in chemical or mineralogical equilibrium suggest that cometary materials have experienced little processing since comet formation, suggesting comets represent pristine repositories of the nebular materials from which the solar system was made. Insight into these materials allows us to look backwards in time for clues about the solar system's formation.

(3) Comets analyzed to date do not show clear trends in the chemical abundances or isotopic signatures that would be expected from our current understanding of where they are supposed to have formed. This suggests that there has been significant movement of these planetesimals since their formation. Scientists will need to integrate the results obtained by remote sensing, landing, and return-sample analyses for many more of these small bodies to better understand how they formed and migrated and the role they have played in the distribution of volatiles and organics in the solar system.

ACKNOWLEDGMENTS

We are grateful to Mike Zolensky and Monica Grady for giving us the opportunity to write this review article. We also thank Yoko Kebukawa, Aaron Burton, Friedhelm von Blanckenburg (the *Elements* principle editor), and Jodi J. Rosso (the *Elements* executive editor), for proofreading the manuscript and giving constructive comments. ■

REFERENCES

- A'Hearn MF, Millis RC, Schleicher DO, Osip DJ, Birch PV (1995) The ensemble properties of comets: results from narrowband photometry of 85 comets, 1976-1992. *Icarus* 118: 223-270
- A'Hearn MF and 9 coauthors (2008) Deep Impact and sample return. *Earth, Planets and Space* 60: 61-66
- A'Hearn MF and 33 coauthors (2011) EPOXI at Comet Hartley 2. *Science* 332: 1396-1400
- Altwegg K and 31 coauthors (2015) 67P/Churyumov–Gerasimenko, a Jupiter family comet with a high D/H ratio. *Science* 347, doi: 10.1126/science.1261952
- Bieler A and 32 coauthors (2015) Abundant molecular oxygen in the coma of comet 67P/Churyumov–Gerasimenko. *Nature* 526: 678-681
- Blake D, Allamandola L, Sandford S, Hudgins D, Freund F (1991) Clathrate hydrate formation in amorphous cometary ice analogs in vacuo. *Science* 254: 548-551
- Busemann H and 5 coauthors (2006) Interstellar chemistry recorded in organic matter from primitive meteorites. *Science* 312: 727-730
- Ciesla FJ, Sandford SA (2012) Organic synthesis via irradiation and warming of ice grains in the solar nebula. *Science* 336: 452-454
- Cody GD and 15 coauthors (2008) Quantitative organic and light-element analysis of comet 81P/Wild 2 particles using C-, N-, and O-μ-XANES. *Meteoritics and Planetary Science* 43: 353-365
- De Gregorio BT and 5 coauthors (2011) Correlated microanalysis of cometary organic grains returned by Stardust. *Meteoritics and Planetary Science* 46: 1376-1396
- Dello Russo N, Kawakita H, Vervack RJ Jr, Weaver HA (2016) Emerging trends and a comet taxonomy based on the volatile chemistry measured in thirty comets with high-resolution infrared spectroscopy between 1997 and 2013. *Icarus* 278: 301-332
- Duprat J and 10 coauthors (2010) Extreme deuterium excesses in ultracarbonaceous micrometeorites from central Antarctic snow. *Science* 328: 742-745
- Glavin DP, Dworkin JP, Sandford SA (2008) Detection of cometary amines in samples returned by Stardust. *Meteoritics and Planetary Science* 43: 399-413
- Hässig, M and 35 coauthors (2015) Time variability and heterogeneity in the coma of 67P/Churyumov–Gerasimenko. *Science* 347, doi: 10.1126/science.aaa0276
- 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
- Meech K (2017) Setting the scene: what did we know before Rosetta? *Philosophical Transactions of the Royal Society A* 375, doi: 10.1098/rsta.2016.0247
- Messenger S (2000) Identification of molecular-cloud material in interplanetary dust particles. *Nature* 404: 968-971
- Mumma MJ, Charnley SB (2011) The chemical composition of comets—emerging taxonomies and natal heritage. *Annual Review of Astronomy and Astrophysics* 49: 471-524
- Noguchi T and 13 coauthors (2017) Variation of mineralogy and organic material during the early stages of aqueous activity recorded in Antarctic micrometeorites. *Geochimica et Cosmochimica Acta* 208: 119-144
- Ootsubo T and 9 coauthors (2012) AKARI Near-infrared spectroscopic survey for CO₂ in 18 comets. *Astrophysical Journal* 752, doi:10.1088/0004-637X/752/1/15
- Quirico E and 37 coauthors (2016) Refractory and semi-volatile organics at the surface of comet 67P/Churyumov–Gerasimenko: Insights from the VIRTIS/Rosetta imaging spectrometer. *Icarus* 272: 32-47
- Sandford SA, Allamandola LJ (1988) The condensation and vaporization behavior of H₂O: CO ices and implications for interstellar grains and cometary activity. *Icarus* 76: 201-224
- Sandford S and 54 coauthors (2006) Organics captured from comet 81P/Wild 2 by the Stardust spacecraft. *Science* 314: 1720-1724
- Sandford SA, Bera PP, Lee TJ, Materese CK, Nuevo M (2015) Photosynthesis and photo-stability of nucleic acids in prebiotic extraterrestrial environments. *Topics of Current Chemistry* 356: 123-164
- Taylor S, Brownlee DE, Flynn GJ (eds) (2016) *Cosmic Dust*. *Elements* 12: 165-202
- Yabuta H and 16 coauthors (2017) Formation of an ultracarbonaceous Antarctic micrometeorite through minimal aqueous alteration in a small porous icy body. *Geochimica et Cosmochimica Acta* 214: 172-190 ■