

Ice to Meet You: Sampling Cold Bodies

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Banner image. Photograph of comet 12P/Pons-Brooks as taken by Dan Bartlett in April 2024. Used with permission.

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ABSTRACT

Icy materials are dispersed throughout the Solar System, from the planets, to their moons, and to asteroids and comets. The volatiles contained within these icy reservoirs could provide vital insights into the origin and evolution of their parent bodies, as well as details of conditions in the early Solar System. The collection of volatile constituents in sample return missions has therefore been given a high priority for the current decade. In this chapter, we describe volatile materials and ices in the Solar System, with a focus on comets. We summarize the history of cometary exploration, describe the results of NASA's *Stardust* mission to comet 81P/Wild 2, and discuss the future of comet sample return.

KEYWORDS: ice; volatiles; comets; Solar System; missions

INTRODUCTION

Volatiles Across the Solar System

Volatiles are molecules that convert between solid and gas phases at low temperatures in vacuum (typically below 200 K). Sublimation points are used to define boundaries, or “snowlines,” in a protostellar disk where volatiles sublime on one side of the snowline and condense to form stable solids (ices) on the other (FIG. 1). Volatiles generally consist of small (< 50 atomic mass units), often hydrogenated, molecules, based on the abundant elements carbon, nitrogen, and oxygen (some abundant volatiles are listed in FIG. 1). Determining the distributions of volatiles within the Solar System is important for informing models of planet formation and migration theory, understanding planetary evolution, and interpreting observations of exoplanets. Volatiles are highly abundant in the solar nebula and represent key drivers of its overall chemistry. The chemical and isotopic contents of ices in comets, asteroids, moons, centaurs, and trans-Neptunian objects help to identify the Solar System's starting materials, as well as constrain protoplanetary disk processes and volatile delivery to terrestrial planets early in Solar System formation. For example, the coexistence of water (volatile) and organic carbon-based molecules is considered critical for the emergence of life and for the habitability of planetary environments.

Although some information on planetary volatiles can be obtained from sensitive and precise analyses of meteorites and interplanetary dust particles (IDPs; some of which are of cometary origin), alteration, exchange, and lack of context mean we must turn to less-sensitive methods, such as telescopic observations and in situ spacecraft instrumentation. Targeted collections of IDPs in the

stratosphere by high-altitude NASA aircraft during the crossings of comets 55P/Tempel-Tuttle and 26P/Grigg-Skjellerup may contain cometary samples. However, it is challenging to distinguish these from the general flux of cosmic dust.

The value of sample return missions is therefore paramount to the understanding of volatiles in the Solar System. Despite the complexity of sample return, a number of these missions—including *Stardust*, *Hayabusa2*, and *OSIRIS-REx*—have provided and continue to provide profound progress in tackling key scientific questions in planetary science. A key advantage of having these returned samples carefully curated is the broad range of studies that can be done by laboratory instrumentation on Earth using current technologies and those yet to be developed (Barnes and Davidson 2025 this issue). Terrestrial laboratories can also provide much more sensitive measurements than are achievable by spacecraft instruments (see FIG. 1 from Milam et al. 2021). While all of this is true, nearly all sample return missions to date have returned only rocky materials made up of, at best, a tiny fraction of volatile compounds.

Returning volatiles from planetary bodies poses unique and severe technical challenges over the return of rocky materials, challenges that depend on the temperature and pressure requirements of the analytes, the mechanisms by which they are collected and stored, as well as levels of preservation to avoid chemical alteration after collection or during the entry, descent, and landing (EDL) phase of a sample return mission.

In this chapter, we discuss the history, challenges, and promising future of returning volatile materials and ices from the surfaces of planetary bodies, with a focus on comets.

Protoplanetary Disks and Snowlines

The primordial elemental composition of the protoplanetary disk of the Solar System is inferred from measurements of the solar atmosphere. Observed or measured compositional, especially isotopic, differences in primitive planetary materials, such as those present in comets and meteorites, are usually understood and explained as the result of processes taking place during the formation and evolution of the Solar System (Pontoppidan and Blevins 2014). Understanding the relative amounts of reprocessed and primordial, or unaltered, materials involves the measurement of volatile isotopes of the four most abundant and chemically reactive elements: C, H, O, and N (“CHON”).

ICY BODIES

Icy surfaces typically exist on planetary bodies found beyond the main asteroid belt, where temperatures are sufficiently low for H₂O ice to be stable. Some examples include the satellites of Jupiter and Saturn, or more-distant worlds such as Pluto and Charon. However, the cold conditions required for ice also can be met in isolated regions of the inner Solar System, such as in the polar caps of Mars, in permanently shadowed craters on the Moon, or even at the poles of Mercury. Here, we focus on comets, objects that originate in cold regions of the protosolar disk, possess orbits that take them far from the Sun, but may be driven into the inner Solar System by gravitational interactions. When visible from the surface of Earth, they often appear in the sky with elongated tails of sublimated gases and dust particles stretching away from a bright nucleus.

Remote and In Situ Observations of Comets

Much of our knowledge of cometary volatile compositions comes from their coma gases observed by ground- and space-based telescopes such as the Atacama Large Millimeter Array (ALMA), the Keck Observatory, NASA's Infrared Telescope Facility (IRTF), as well as the *Spitzer*, *Hubble*, and *James Webb* space telescopes. Such observations have provided long-term monitoring of a plethora of comets across a range of different wavelengths, where each part of the spectrum probes different locations and chemical processes in the coma, revealing the presence of different chemical origins. Before the European Space Agency (ESA)'s *Rosetta* mission, these remote observations routinely detected an inventory of over two dozen volatile species in cometary comae. New observatories with improved technology have since helped expand this number, as well as provide access to fainter, and even more distant, objects.

Valuable insights into comet geology, composition, and activity have also been provided by the handful of missions to comets, which have performed in situ analyses (TABLE 1; FIG. 2). In particular, the missions to comets 1P/Halley, 9P/Tempel 1, 103P/Hartley, and 67P/Churyumov–Gerasimenko discussed here, and to 81P/Wild 2 discussed in the next section. Comet 1P/Halley, a short-period comet (passing through the inner Solar System roughly every 76 years) was greeted on its most-recent apparition in 1986 by the so-called “Halley Armada”—an international fleet of spacecraft that together performed analyses of the comet throughout that year. They revealed the structure of jets near the nucleus, and they also collected the first close-up images of a cometary nucleus, showing fine details of the surface and revealing a very low albedo. In addition, several spacecraft were equipped with mass spectrometers to measure the composition of Halley's dust grains (Kissel et al.

1986; Fomenkova et al. 1992). Three distinct grain types were identified: those dominated by CHON particles, those dominated by silicates, and those that were a mixture of the two.

In 2005, NASA's *Deep Impact* mission arrived at comet 9P/Tempel 1. The spacecraft observed chemical diversity across the comet's surface; for example, H₂O and CO₂ ices were unevenly distributed. A key component of this mission was the 100-kg copper impactor it carried, used to excavate fresh nucleus material for study. Analyses of the impact plume it created revealed the presence of abundant organic molecules, supporting the notion of comets as seeders of Earth's early chemistry (A'Hearn et al. 2005). There also were coordinated efforts to observe the impact event, and for example, the *Spitzer* space telescope obtained infrared spectra that suggested the presence of carbonate and clay minerals; their formation, requiring reactive liquid water, was unexpected in a comet (Lisse et al. 2006). The *Deep Impact* spacecraft remained in good health and was approved for another flyby of Comet 103P/Hartley, providing significant detail on the heterogeneous nature of this bi-lobed comet.

In 2014, ESA's *Rosetta* mission arrived at comet 67P/Churyumov–Gerasimenko, becoming the first spacecraft to orbit a comet. Its instruments and those of the *Philae* lander probed the comet's composition, revealing it to have a very dark surface rich in non-volatile organics (Capaccioni et al. 2015). Based on infrared reflectance measurements, the comet was found to include carboxylic acids, and from mass spectrometry, ammoniated salts (Altwegg et al. 2020). The coma of 67P/Churyumov–Gerasimenko also contained high abundances of molecular oxygen. The coma's D/H ratio was initially estimated to be higher than that of other comets in similar orbits, the so-called Jupiter-family comets (JFCs), leading to doubt as to whether such comets could be the source of Earth's seawater (Altwegg et al. 2015). However, modeling by Mandt et al. (2024) showed that the coma's D/H ratio may be affected by the process of sublimation from icy dust grains, and the D/H ratio of the bulk ice in 67P/Churyumov–Gerasimenko may be lower than measured in the coma gas and, thus, similar to that of terrestrial water and other JFCs.

THE STARDUST MISSION

Overview

As well as conducting in situ observations of 81P/Wild 2 in 2004, NASA's *Stardust* mission performed the first, and as yet only, sample return of cometary materials (Brownlee et al. 2006). The cargo, returned in 2006, held dust grains released from the comet's nucleus and captured by *Stardust*'s

racket-like collector (FIG. 3A). Efforts were made to minimize the encounter speed, and ultimately the grains impacted the collector at approximately 6 km s^{-1} ($21,600 \text{ km h}^{-1}$). Collisions with most materials at such speeds cause intense heating and pressure, resulting in disruption, melting, and vaporization, such that the original composition and structure are modified or even lost. Therefore, as its primary capture medium, Stardust's collector incorporated aerogel—an ultra-low-density, highly porous, silicon-based glass—which had been used in the laboratory and on orbital flights to gently decelerate and capture hypervelocity particles (e.g., Tsou et al. 2003; Burchell et al. 2006). Stardust's aerogel cells were held in a metal frame by aluminum foils that served as a secondary capture medium. Cometary particles impacting the aerogel were preserved as fragments along and at the ends of tracks (FIG. 3B), whilst those impacting the foils were preserved as residues that lined craters in the aluminum (FIG. 3C).

At the time of sample collection, 81P/Wild 2 was a relatively new visitor to the inner Solar System, having been perturbed into its 6.2-year orbit by an encounter with Jupiter in 1974 (Sekanina 2003). Such fresh cometary nuclei were believed to have experienced minimal changes since accretion, and it was therefore anticipated that the samples would preserve a snapshot of pristine early outer Solar System materials—a mix of ices and organics, with abundant amorphous materials originating from the interstellar medium and microscopic crystals including many that should predate the Solar System itself, having originated around other stars. Analyses to date indicate materials derived from aqueous alteration or thermal metamorphism are rare in 81P/Wild 2 and, therefore, the samples were well preserved in the cold outer reaches of the Solar System as expected. However, rather than being dominated by amorphous materials, the samples are instead comprised of abundant and varied crystalline anhydrous silicates, with many larger ($> \mu\text{m}$) sized particles similar to meteoritic chondrules (Nakamura et al. 2008), fragments of calcium-aluminum-rich inclusions (Simon et al. 2008), and most recently an entire chondrule (Joswiak et al. 2024). Such high-temperature components were not expected because they are believed to only form in the inner Solar System near the Sun. Their presence in the outer system would require an efficient method of transport and mixing of inner and outer system materials or a local heating mechanism, which overturned earlier theories of comet formation and conditions in the early outer Solar System and triggered significant study of the migration of chondritic components.

Limitations and Lessons Learned from Stardust

The Stardust aerogel and foils remain our only example of returned samples from a comet and are still being studied. The total mass of material returned was $\sim 1 \text{ mg}$ —an extremely small amount

compared with lunar and asteroidal sample return missions—and in the form of minute particles distributed over the entire collection surface (aerogel and foil, 1191 cm² in area). Initial surveys identified the locations of the larger tracks and craters, but in-depth studies required the development of time-consuming methods to retrieve the cometary materials from aerogel (Westphal et al. 2004; Ishii et al. 2005), or the flattening of craters to lift residues for extraction by a focused ion beam (Wozniakiewicz et al. 2018). As a result, although efforts continue, there are currently limited statistics upon which to base interpretations.

Capture via impact was a necessary and highly ingenious method for sample return, however, grains were ultimately subject to alteration: impacts into the foils resulted in pressures >10 GPa, peak post-shock temperatures >1000 °C, and extensive melting and vaporization (Burchell et al. 2009). In the aerogel, even with reduced pressures (~100 MPa), particles exhibited melt rims comprising a mixture of the particle and aerogel, and ablated particles were observed along the lengths of tracks (Hörz et al. 2006). Efforts made to study impact analogues created under simulated encounter conditions can guide our interpretations of original cometary characteristics from the *Stardust* samples (e.g., Kearsley et al. 2007). They also highlight where we must remain cautious. For example, presolar grain abundances are modified (decreased) by impact, as demonstrated by Floss et al. (2013).

The measurement of organics was a secondary goal of the mission. They have been identified in *Stardust* samples but have required the application of high-mass-resolution techniques and the measurement of isotopic signatures to prove a cometary origin, as in the case of Elsila et al. (2009) who identified cometary glycine in the returned aerogel. Such precision is necessary, as organics were altered during the collection process, and the method of aerogel manufacture itself involves organic solvents. Thus, contamination is an unavoidable issue that has limited the range of organics identified to date (Sandford et al. 2010).

Stardust was the first, and remains the only, sample return from a comet, and the samples have permitted in-depth analyses of cometary dust. However, the icy, volatile component remains unsampled, meaning that our knowledge of the composition of icy bodies remains incomplete and new missions to comets are needed to understand cometary volatiles. Further, the *Stardust* samples represent only a single comet—Wild 2—raising the question of whether it is representative of comets or icy bodies in general. Sample return from more comets will provide more insight.

FUTURE MISSIONS TO COMETS

The connections of comets 81P/Wild 2 and 67P/Churyumov-Gerasimenko to asteroids and meteorites are still unclear (Yabuta et al. 2025 this issue). Answers may be provided by the collection and return of cometary dust, volatiles, and ices to laboratories on Earth, leading to information about the origin and distribution of volatiles throughout the Solar System. By studying the isotopic and chemical compositions of cometary ices, the origin and chemical evolution of these compounds and their original volatile reservoirs (whether they originated in the interstellar medium or the protoplanetary disk) can be determined. The isotopic compositions of oxygen in volatile compounds like H₂O and CO, abundant in cometary ices, are particularly useful for these studies.

Not only could cometary ices inform us about their own histories and that of the early protosolar disk, but studies of cometary H₂O can be used to understand the origins of Earth's oceans and whether comets were a contributing source of Earth's water. The delivery of cometary volatiles and organics early in the history of Earth has significant implications for the origin of prebiotic chemistry and the origin of life itself. This could also be tested with a returned cometary sub-surface sample in a modern analytical laboratory.

Proposed Comet Sample Return Missions

The document "Origins, Worlds, and Life: A Decadal Strategy for Planetary Science and Astrobiology 2023–2032" (National Academies of Science, Engineering, and Medicine 2023) outlines Priority Science Questions that should be addressed by a comet surface sample return mission proposed in the next 10 years. These include understanding the evolution of the protoplanetary disk of the Solar System, from its initial conditions, to the separation of gas and solids into distinct reservoirs, and to the condensation of protoplanetary materials into planetesimals (including comets and asteroids) and further into larger planets and planetary bodies. Comet surface sample return could provide clues to the means by which a small body like an asteroid or comet incorporates and retains volatiles since the time of its formation.

However, returning a sample from an icy body such as a comet is challenging. Comet nuclei are small (about 4 km in size or smaller), with a dynamic coma full of gas, dust, and ice particles (as shown by *Rosetta*). Their surfaces are heterogeneous mixtures of dust and ice at temperatures of 100–150 K and lower, occasionally emitting jets of volatile gases. Sampling of this type of surface has not yet been demonstrated by a space mission. Even if a sample were to be successfully collected and stored

in the spacecraft for the long return to Earth (estimated to be 5–10 years for some well-studied targets), sample preservation through the return and EDL phases of a mission timeline presents challenges of its own. Once the flight and EDL phases of the mission are completed, long-term sample curation must be implemented. Several comet surface sample return missions were proposed to the fourth cycle of NASA's *New Frontiers* program (NF4) in 2017, and each addressed these challenges (and others not mentioned here) in their own ways. Three are described below.

CORSAIR. The *Comet Rendezvous, Sample Acquisition, Investigation, and Return (CORSAIR)* mission (Sandford et al. 2017) was designed to rendezvous with comet 88P/Howell and perform coma and surface characterizations and collect two surface samples. In addition, nine coma gas samples would be obtained at different times in attempt to link the coma and surface compositions. The sample collector would not require landing or touch-and-go (TAG) maneuver and instead would use a ballista to grab samples from a close flyby of the nucleus. Gases produced by the sublimation of volatiles within the samples would be analyzed by mass spectrometry on the return cruise.

CONDOR. The *COmet Nucleus Dust and Organics Return (CONDOR)* mission (Choukroun et al. 2017) was proposed to retrieve a sample of surface material from comet 67P/Churyumov-Gerasimenko. It would collect and return a >50-g sample using its BiBlade sampling tool, which could be capable of acquiring up to 590 cm³ of material. The sample would then be contained in two compartments of a return capsule, where molecular sieves in the lids would capture released volatiles for later analysis. The sample would be maintained at <293 K for the return cruise and Earth re-entry.

CAESAR. The *Comet Astrobiology Exploration Sample Return (CAESAR)* mission goal in NF4 (Hayes et al. 2018) was to rendezvous with comet 67P/Churyumov-Gerasimenko, map its surface to look for changes since the *Rosetta* mission, and to collect >100 g of cometary surface materials. The sampling system designed for *CAESAR* drew upon the heritage of the *OSIRIS-REx* mission to asteroid Bennu (Yabuta et al. 2025 this issue), in that its TAG collection would consist of a sampling head at the end of a robotic arm, where surface ice and dust would be blown into the collector using on-board tanks of nitrogen gas. Once collected, the volatiles (including H₂O) would be separated from the minerals and refractory organics by trapping them in a second volume called the Gas Containment System (GCS). Once separated, the GCS would be sealed, and the refractory grains would be outgassed by venting into space during the return cruise, preventing alteration by prolonged contact with H₂O vapor or other gasses.

Other comet mission concepts. The ESA/JAXA *Comet Interceptor* mission, to be launched in 2029, could provide the first encounter with a long-period comet or interstellar object, sampling the coma

for plasma, dust, and gas (Snodgrass and Jones 2019). *AMBITION*, proposed to ESA's *Voyage 2050* program aims to return a cryogenic sample from a comet or other small planetary body (Bockelée-Morvan et al. 2019). The *Next-Generation small-body Sample Return (NGSR)* concept by JAXA would return a non-cryogenic sample of subsurface cometary dust from a JFC, with volatile analyses performed in situ (Sakatani et al. 2025).

The return of true cryogenic samples (<77 K) from a variety of locations throughout the Solar System is highly desired, because of the potential to bring the most volatile and pristine materials to Earth for study. However, the technologies required to collect, contain, return, curate, and analyze such samples are still in development and can be prohibitively expensive for the New Frontiers class of missions. Hence it is unclear whether cryogenic sample return will be possible within the upcoming NF5 opportunity. Rather, technological development is likely to occur in stages—the first of which could be the return of cold samples from lunar permanently shadowed regions, with cometary surface samples to follow.

SUMMARY

The return of volatile samples in either gas or solid form has the potential to revolutionize our understanding of the Solar System and the early Solar nebula and is needed to fill in the knowledge gaps about volatile compounds in the Solar System. This is recognized widely as a top priority for the current decade of space mission development. Furthermore, the return of cometary samples has already been an ongoing effort of technology and engineering spanning many years, with flybys through the coma of 1P/Halley in 1986 to measure its gas and dust content in situ, to the capture and return of dust particles from the coma of 81P/Wild 2 in 2004 by the *Stardust* mission, to (most recently) the close-orbiting *Rosetta* spacecraft and lander in 2015 to study the nucleus of comet 67P/Churyumov-Gerasimenko. The future of comet sample return may rely on the return of non-cryogenic (>77 K) volatile samples in the next decade mission proposals, upon which the ultimate goal of cryogenic (<77 K) sample return from a comet may be achieved.

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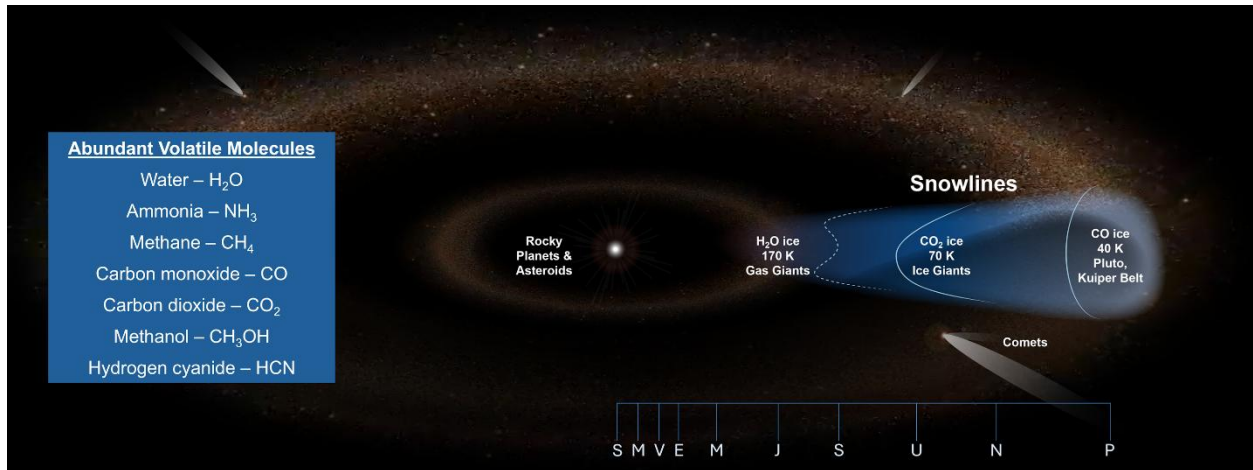


Figure 1: Frozen volatiles (“ices”) exist in protoplanetary disks where the distance from the central star allows the temperature to fall below the sublimation point for the solids in a vacuum (“snowlines”). H₂O ice in the Solar System is stable from the gas giant planets (Jupiter and Saturn) and beyond, solid CO₂ outward from the ice giants (Uranus and Neptune), and solid CO is present on surfaces starting at about the distance of Pluto and the Kuiper Belt. Comet families originate from these low-temperature regions in the early Solar System. Abundant cometary volatiles include the simple compounds of H, C, N, and O that are listed. The approximate distribution of the Sun, planets (Mercury, Venus, Earth, Mars, Jupiter, Saturn, Uranus, and Neptune), and Pluto within the Solar System is indicated. (Note: distances are not to scale.)

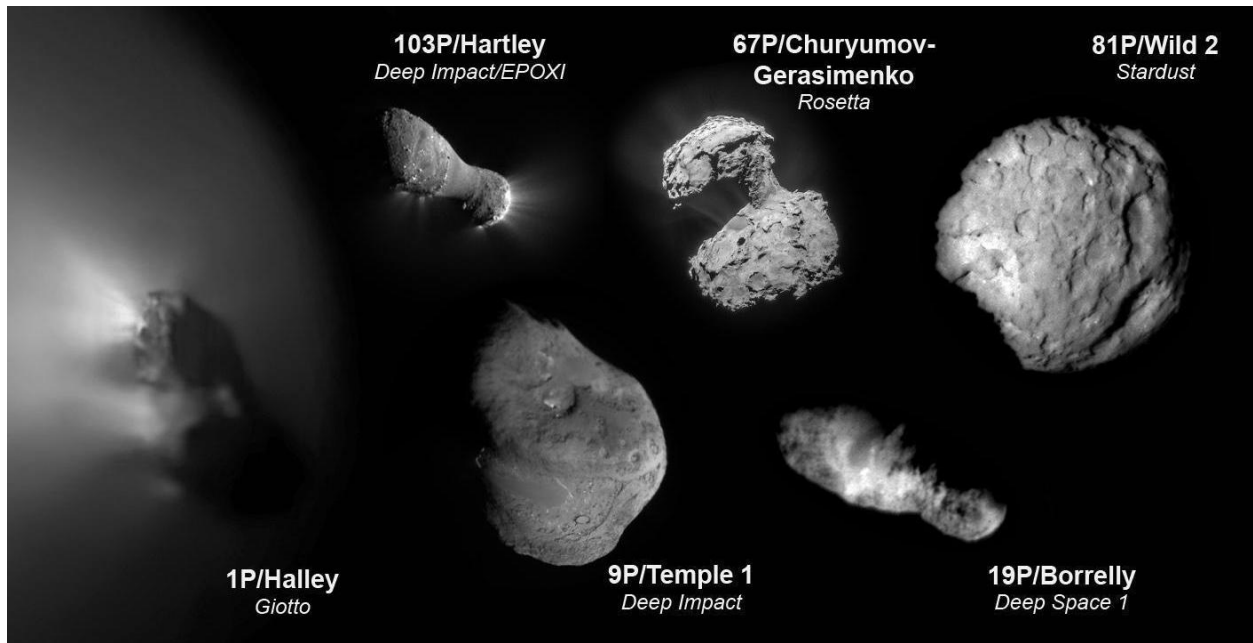


Figure 2: Montaged image of all cometary nuclei visited and imaged to date by spacecraft (not to scale). Two further comets have been visited by spacecraft but not imaged: 21P/Giacobini-Zinner and 26P/Grigg-Skjellerup. INDIVIDUAL IMAGE CREDITS: 1P/HALLEY, ESA/MPS; 19P/BORRELLY, NASA/JPL; 103P/HARTLEY, NASA/JPL-CALTECH/UMD; 9P/TEMPEL 1, NASA/JPL/UNIVERSITY OF MARYLAND; 81P/WILD 2, NASA/JPL-CALTECH; 67P/CHURYUMOV-GERASIMENKO, ESA/ROSETTA/NAVCAM.

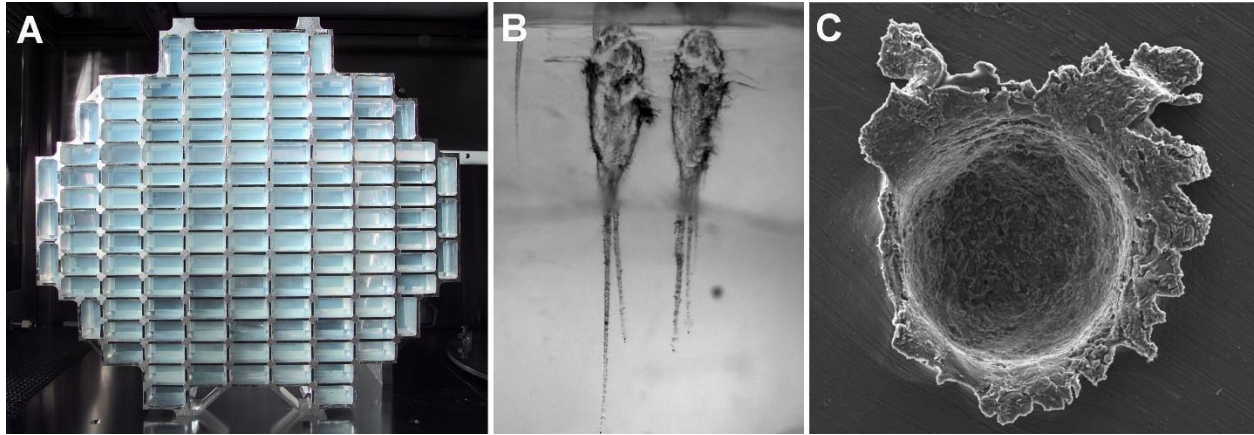


Figure 3: *Stardust* sample return from comet 81P/Wild 2. (A) The *Stardust* cometary collector tray, comprising aerogel cells held in a metal frame by aluminum foils. IMAGE CREDIT: NASA/ JPL/CALTECH. (B) A pair of tracks (69 and 32, 11 and 8.5 mm long, respectively) in aerogel cell C2072 with remains of the impacting cometary particles preserved along and at the ends of the tracks. IMAGE CREDIT: NASA/JPL-CALTECH/UNIVERSITY OF WASHINGTON. (C) A crater $\sim 40 \mu\text{m}$ in diameter found on aluminum foil C2104W containing residue of the impacting cometary particle. IMAGE CREDIT: A. KEARSLEY/NATURAL HISTORY MUSEUM, LONDON.

TABLE 1: EVERY COMETARY NUCLEUS VISITED BY SPACECRAFT TO DATE.

Comet	Mission - Agency	Mission type	Closest approach date	Closest approach distance (km)
21P/Giacobini-Zinner	<i>International Cometary Explorer (ICE)</i> - NASA	Flyby	1985	~7800
1P/Halley	<i>Vega 1</i> - USSR	Flyby	1986	8,890
	<i>Vega 2</i> - USSR	Flyby	1986	8,030
	<i>Sakigake</i> - ISAS/JAXA	Flyby	1986	7,000,000
	<i>Giotto</i> - ESA	Flyby	1986	596
	<i>Suisei</i> - ISAS/JAXA	Flyby	1986	151,000
26P/Grigg-Skjellerup	<i>Giotto</i> - ESA	Flyby	1992	200
19P/Borrelly	<i>Deep Space 1</i> - NASA	Flyby	2001	2171
81P/Wild 2	<i>Stardust</i> - NASA	Flyby, sample return	2004	236
9P/Tempel 1	<i>Deep Impact</i> - NASA	Flyby	2005	500
	<i>Deep Impact</i> - NASA	Impactor	2005	Touchdown
103P/Hartley	<i>EPOXI</i> - NASA	Flyby	2010	694
67P/Churyumov-Gerasimenko	<i>Rosetta</i> - ESA	Orbiter	2014	Touchdown
	<i>Rosetta/Philae</i> - ESA	Lander	2014	Touchdown

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