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Return to Wild 2

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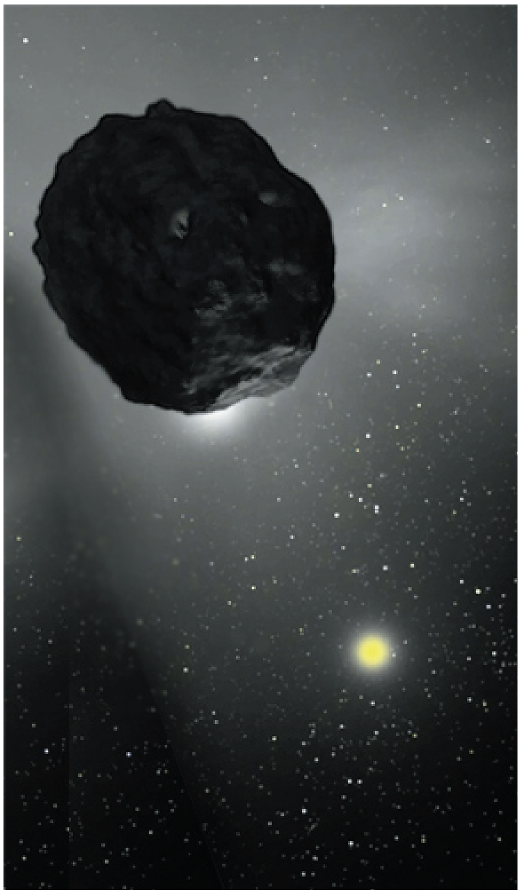

On its encounter with Comet Wild 2 in January, 2004, the Stardust spacecraft flew through a cloud of dust and gas.
(Courtesy NASA/JPL-Caltech)

NASA's Stardust mission was the first to bring back pristine samples of a comet and the first to return dust particles directly from interplanetary space. It would not have been surprising if these materials had given evidence of a shared origin—a very cold one at that.

In fact the early results from Stardust's Preliminary Examination Teams (PETs), reported in *Science* magazine in December, 2006, were full of surprises. As Stardust principal investigator Don Brownlee said, shortly after scientists had taken their first peek at the samples, "We have found fire and ice. In the coldest part of the Solar System, we have found samples that have formed at extremely high temperatures."

The apparent anomaly of the comet's origins was vividly displayed in the analysis of Stardust's carbon-based compounds as initally reported by the organics Preliminary Examination Team. Stardust's unusual mix of organics has now been revisited in a detailed study to be published in the journal *Meteoritics and Planetary Science*.

"This comet is god-awful complex," says geophysicist George Cody of the Carnegie Institution of Washington, corresponding author of the new paper. "It contains materials that have no business being together, compounds with completely different histories."

Astrophysicist Scott Sandford of NASA Ames Research Center, who led the PET study of organics published in *Science*, says, "The compounds we see were processed all over the Solar System and passed back and forth, mixing like a giant washing machine. Some mineral components are among the highest-temperature minerals you can make. Others, including some of the organics, are so volatile it's remarkable they survived capture."

Wild 2's wild mix of constituents begs for an explanation. Theories of the early Solar System dating back to before Stardust had attempted to explain the presence of high-temperature minerals like calcium aluminum inclusions (CAIs) and chondrules, or resolidified molten droplets of silicates, in carbonaceous meteorites. But none of these models is without problems.

"One is the X-wind model," says Cody, "which proposes that the material drawn near the center of the rotating protosolar disk got hot enough to melt or vaporize. This high-temperature material was then ballistically launched out into the cold regions of the Solar System, far from the young star." Other models are less violent: some invoke a spiraling path for the material around the newly forming Sun, so that it experienced temperatures that varied with distance from the plane of the ecliptic. Others explain temperature changes

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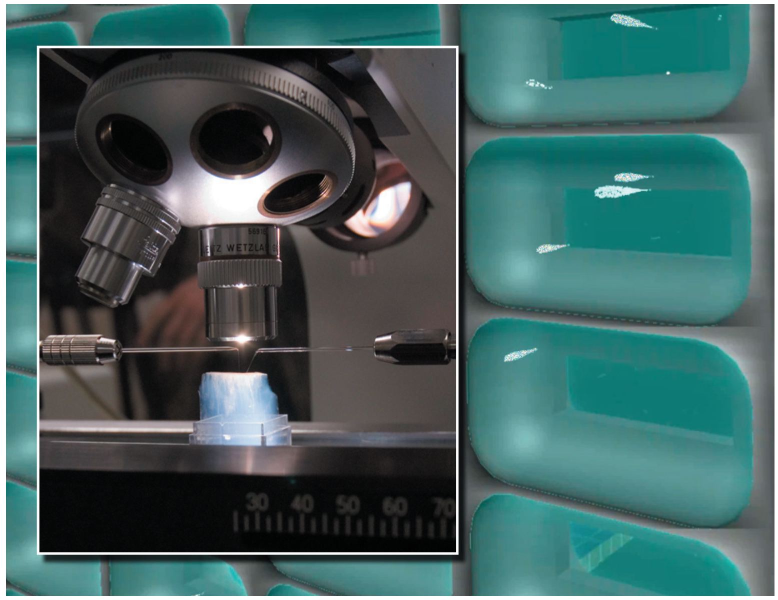
on the basis of dynamic variations of pressure and momentum in the solar nebula. The challenge for the organics team is to use the evidence of the compounds in the Stardust samples themselves to select the best model.

"How common are the high-temperature particles?" asks Sandford. "If the models can predict the mixing ratios of the different kinds of particles, we may be able to choose among them. Whatever the model, there will be a reality it has to match."

Samples and tools

To collect comet particles, Stardust aimed a grid of aerogel tiles shaped something like a tennis racket toward the comet as the spacecraft flew past in January, 2004. At other times during the seven-year mission, Stardust used the opposite side of the aerogel grid to attempt to collect particles of interstellar dust.



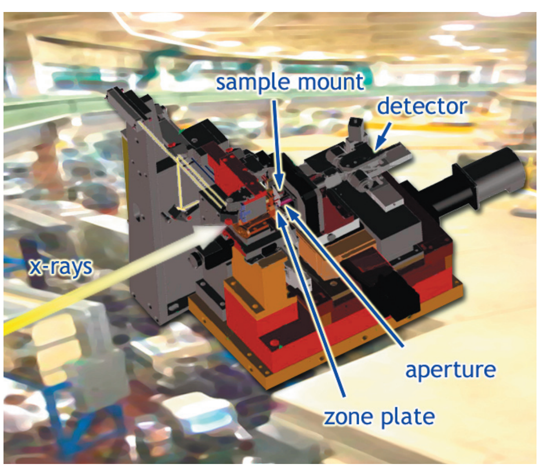
Difference in orbital speed between the comet and the spacecraft caused particles to strike Stardust's silica aerogel collector at hypervelocity. Particles and segments of the aerogel surrounding them were extracted by robotic instruments (inset).

(Courtesy NASA/JPL-Caltech)

The tiles of wispy aerogel, a thousand times less dense than glass, were designed to capture the material as gently as possible. Nevertheless, with comet grains slamming into the gel six times faster than a rifle bullet, significant impact forces, friction, and heat were inevitable.

As they braked to a halt, the captured particles left long carrot-shaped tracks in the translucent gel, often shedding fragments and volatile compounds on the way in. Although altered much less than the outer portions of meteorites, and probably less than most interplanetary dust particles collected in Earth's atmosphere, heat effects were still significant.

"The question is, how hot did the organics get, and how long did they stay hot?" Cody says. "A lot of heating means some chemical processing."



Two STXM beamlines at Berkeley Lab's Advanced Light Source, beamline 11.0.2 and 5.3.2 (whose end station is pictured here), were among the principal instruments used to analyze Comet Wild 2's organics

The researchers cut out "keystones" of aerogel surrounding the tracks; individual particles were removed with sterile glass needles. The aerogel itself was inspected for gases, either gases that the comet had directly sublimed into space or gases that had vaporized from volatile organics, heated when the solid fragments were captured.

The samples were fixed in epoxy or pure sulfur, then sliced less than 150 nanometers thick (150 billionths of a meter) with a diamond knife. The organics team analyzed nine particle samples, including two pieces of a single particle sliced in different places.

The instruments of choice for analyzing Stardust's organics were STXMs ("sticks-ums"), scanning transmission x-ray microscopes, which use very high-brightness radiation from synchrotrons. Of the three STXMs used in the study, one was at Brookhaven National Laboratory's National Synchrotron Light Source and two were at Berkeley Lab's Advanced Light Source, those on beamline 5.3.2 and beamline 11.0.2.

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The organics team used the STXMs for x-ray absorption near-edge structure, or XANES, which pinpoints atoms of individual elements by probing their core electrons at distinctive energies. The microfocusing capability of the scanning microscopes enabled the identification of different organic domains separated by only tens of nanometers from one another.

The researchers used micro-XANES (µXANES) to reveal the presence and abundance of carbon, nitrogen, and oxygen functional groups in the Stardust samples. The rich assortment of carbon functional groups in the various particles included quinone, aromatics, olefins, vinyls, enol, aliphatics, carboxyls, alcohols and ethers, carbonates, and others. Nitrogen functional groups included imine, nitrile, amines, urea, and more; organic oxygen groups were studied in less detail but included ketone, carboxyl, alcohols and ethers, and enols.

The task facing the investigators was not only to determine the relative abundance of these organic functional groups in the Stardust particles, but to compare that data with what was already known from studies of other extraterrestrial materials, particularly the meteorites known as carbonaceous meteorites. Meaningful comparisons crucially depend upon understanding what alterations occurred when the Stardust samples were captured and prepared.

Alteration and contamination

Sandford was on the Stardust team that recovered the sample-return capsule when it parachuted into the Utah desert in January, 2006. Contamination control was a special worry for the organics team.

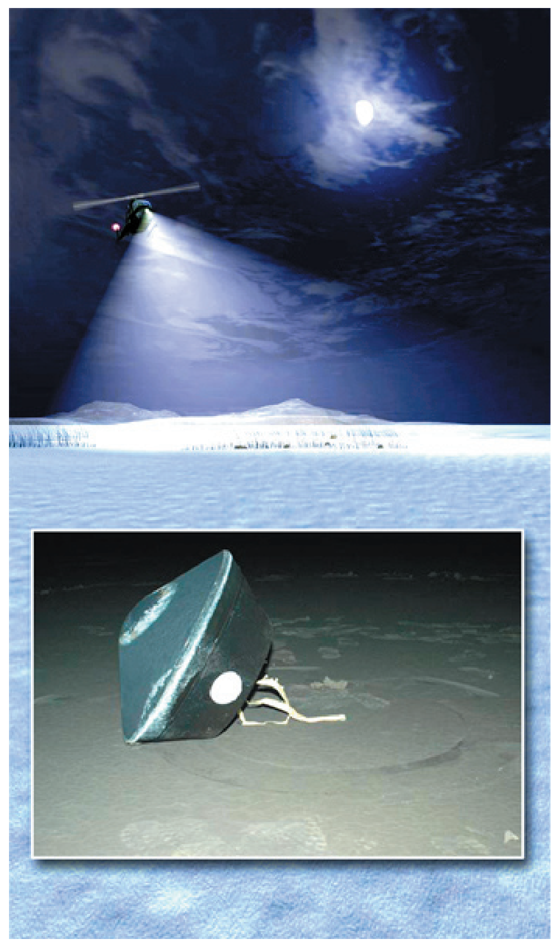
“We worked to eliminate or identify any contamination when the spacecraft was built, while it was in flight, when it reentered the atmosphere, and especially after it hit the ground,” Sandford says. “I collected samples of all the organic compounds near the landing site, including samples of the soil the capsule came to rest in.”

Of the possible sources of organic contamination, the one that proved significant came from the aerogel tiles themselves, which were made from organosilica precursors. Silicon and carbon contamination from the aerogel had to be estimated precisely before elemental ratios of nitrogen and oxygen to carbon could be determined for the samples.

Says Cody, “Samples that had been mounted in epoxy exhibited an interesting organic phase, that in essence resulted from a reverse contamination: a carbonaceous phase intrinsic to the Stardust particles had been dissolved and extracted by the epoxy.” By comparing a carbon-XANES spectrum of pure epoxy to the signal from the sample, this soluble phase was readily shown to be different from any known contaminant. “Thus it may constitute soluble cometary organic matter,” he says.

The intense x-ray beam of synchrotron radiation may also produce artifacts, for example by generating energetic secondary electrons that change some chemical groups into others. This phenomenon is well known from previous STXM studies of carbonaceous meteorites.

“Consequently,” Cody says, “the detection of vinyl-keto groups in the Stardust samples is convincing evidence that the comet organic matter contains sugar-like molecules.”



The Stardust sample-return capsule landed in the mud of a dry lake bed at the US Air Force’s Utah Test and Training Range at 3:10 a.m. on January 15, 2006.

(Courtesy NASA/JPL-Caltech)

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Taking all of these observations into account—including consideration of the potential for alteration during the split-second capture of the particles—the difference between the Stardust samples and the previously studied meteorites stood out boldly.

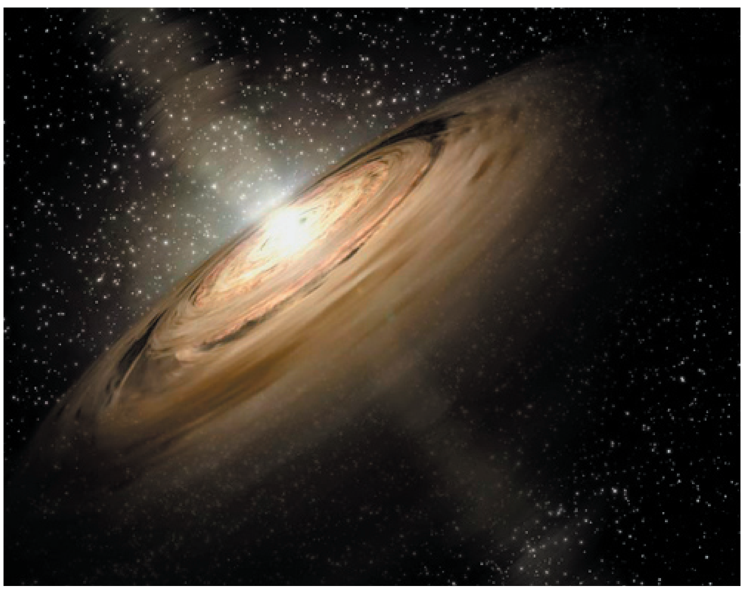
"Unlike meteorites, it's clear that the elemental chemistry of the organics from the comet vary to a spectacularly large degree," says Cody. Studies of the comet's mineralogy and chemistry point to the same conclusion as the organics studies: there is no single precursor to the organics in the comet, no uniform molecular cloud from which the comet condensed. Exactly where the different components of the comet were formed is still far from clear, however.

Not the end of the story

Nitrogen, oxygen, sulfur, and other elements besides carbon and hydrogen contribute to the wide variety of atoms found in the comet's rich inventory of organic functional groups, a variety evident even though samples from only eight different particles were studied. It is too soon even to guess at the "average" organic structure of Wild 2; many more samples will have to be analyzed before a pattern emerges.

Until then, the celestial origin of the many chemical compounds in the comet cannot be determined, and which of the many theories about how comets were formed in the early Solar System is the right one—or which combination of theories—can't yet be decided.

"The Preliminary Examination Teams are not the end of the Stardust story," Cody says, "I'd guess it will take us five more years of study before we've learned everything Wild 2 has to tell us about organics in the early Solar System."



Stardust results suggest the early Solar System was even more complex than theorists have assumed.

(Courtesy NASA/JPL-Caltech)

Additional information

"Quantitative organic and light element analysis of Comet 81P/ Wild 2 particles using C-, N-, and O-µ-XANES," by George D. Cody, Harald Ade, Conel M. O'D. Alexander, Tohru Araki, Anna Butterworth, Holger Fleckenstein, George Flynn, Mary K. Gilles, Chris Jacobsen, A. L. D. Kilcoyne, Keiko Messenger, Scott A. Sandford, Tolek Tyliszczak, Andrew J. Westphal, Susan Wirick, and Hikaru Tabuta, will appear in *Meteoritics and Planetary Science* (MAPS).

More about analysis of Comet Wild 2 samples at the ALS is at http://www.lbl.gov/Science-Articles/Archive/sabl/2007/Jan/ALS-comet.html.

More about analysis of meteorites and interplanetary dust grains using ALS beamline 5.3.2 is at http://www.lbl.gov/Science-Articles/Archive/sabl/2005/August/03-it-came.html.

More about the Stardust mission is at http://stardust.jpl.nasa.gov/home/index.html.