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Development of Integrated Microanalysis of Nanomaterials (06-ERI-001)

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Final Report

Introduction: Comets—small extraterrestrial bodies of ice, dust, and small rocky particles—are considered the oldest, most primitive bodies in the solar system. They were thought to be composed of preserved interstellar particles from 4.6 billion years ago, when the Sun and the planets began to form from a primordial disk of dust and gas. The nonvolatile mineral components of comets are probably natural nanomaterials that include preserved interstellar dust as well as the first solids condensed in the solar system. Thus, comet samples may be considered as forensic "time capsules" from the presolar molecular cloud and the earliest stages of solar system formation.

Cometary material was captured in 2004, when the National Aeronautics and Space Administration's Stardust spacecraft flew through the coma of comet Wild as it neared the orbit of Mars. As Stardust approached the 4.5-kilometer-diameter comet, the spacecraft briefly extended a collector filled with lightweight aerogel glass foam to capture thousands of tiny particles. On January 15, 2006, the spacecraft ejected its sample return capsule onto the Utah desert southwest of Salt Lake City.

Researchers at LLNL supported by this LDRD were part of a collaborative team investigating the mineralogical, chemical, and isotopic compositions of natural cometary nanomaterials from the Stardust mission using the unique array of analytical facilities at Livermore. The studies have provided provide new insight into cosmically primitive materials that will enable a better understanding of the earliest stages of disk accretion around stars. The skills and analysis techniques developed for the characterization of these natural nanomaterials are synergistic with several Livermore programmatic needs in the emerging fields of nanomaterials, nanotechnology and forensics. The Stardust samples are also ideal training materials for a new generation of young scientists using state-of-the-art analytical instruments at the Laboratory.

The LDRD team developed an integrated microanalysis capability utilizing advances in detection and imaging capabilities using electron microscopy and ion microprobe techniques with the state-of-the-art instrumentation at Lawrence Livermore to enable a new level of analytical techniques for nanoscale materials characterization that are directly applicable to the Laboratory's missions in stockpile stewardship and homeland security. For example, the techniques used to investigate Stardust samples are now being used to interrogate interdicted materials as part of nuclear forensic efforts to counter nuclear proliferation and terrorism. The project also underscored, to a global audience, the Laboratory's commitment to achieving breakthroughs in fundamental science and applied technology.

Cometary particulates scattered along impact tracks in aerogel and lining the microcrater walls in the aluminum foils of Stardust's collector were subjected to a multitechnique preliminary examination with synchrotron-based x-ray diffraction; nanometer-scale, secondary-ion mass spectrometry; and electron microscopy, and the initial findings were reported in *Science*. Surprising early observations revealed the scarcity of presolar material, the tiny interstellar grains produced around other stars that existed before the Sun and solar system formed. Furthermore, the identification of refractory (stable at high-temperature) mineral grains suggests a much more complex radial mixing of materials in the solar accretion disk than had previously been appreciated.

In 2008, the team conducted light gas-gun shots of mineral grains into aerogel as well as atomic-scale scanning transmission electron microscope studies of Stardust comet grains to determine the degree of alteration experienced by the materials during capture, the mineralogy of Wild-2 dust, the isotopic compositions of Stardust grains, and the bulk and trace element compositions. Researchers found that capture damage to the Stardust samples was significant but that important scientific information can still be found at the atomic scale. The Comet Wild 2 sample did not contain what was expected in a comet. The sample appeared to contain inner solar system materials similar to those found in meteorites (most meteorites are from the asteroid belt in the inner solar system). This totally unexpected finding, after roughly two years of careful examination of the returned sample, essentially redefined the direction of comet science and the thought that formation of the solar system was rather quiet and orderly—the process now appears to have been much more dynamic and violent. A paper describing this surprising finding appeared in Science **319**, 447-451 (2008). In addition, our team coauthored six (6) Stardust papers appeared in the December 15, 2006 issue of *Science*. Three new sample return mission proposals with LLNL science team members, each with a budget of ~$800M, have recently been submitted to NASA's New Frontiers Program. The support we received under this LDRD (06-ERI-001) was instrumental in our participation in these proposals.

The next step in this work is to fully integrate the state-of-the-art analytical instruments: the focused ion beam; field-emission scanning electron microscopy; nanometer-scale secondary-ion mass spectroscopy; and SuperSTEM scanning transmission electron microscopy. This will enable precious samples, whether Stardust or one-of-a-kind nuclear forensics samples, to be analyzed with multiple analytical techniques, thereby maximizing the science yield. These activities have enhanced the international reputation of LLNL in materials science and space sciences and resulted in a high-profile, multidisciplinary project that was attractive to a broad range of researchers and highly successful in recruiting young talented scientists. In addition, it lead to numerous collaborations with academic institutions as well as federal agencies, and the results were reported in high-profile scientific journals.

Figure 12. An artist's conception shows the Stardust spacecraft approaching Comet Wild 2. The spacecraft's cometary particle collector, filled with lightweight aerogel glass foam, is shown extended. The spacecraft is flanked by two solar panels. (Image courtesy of the National Aeronautics and Space Administration.) In the lower right photo, John Bradley gives the thumbs-up sign after scientists opened the Stardust sample return capsule, for the first time, in the clean room facility at the agency's Johnson Space Center.