THE PRELIMINARY EXAMINATION OF ORGANICS IN THE RETURNED STARDUST SAMPLES FROM COMET WILD 2. S. A. Sandford[1], J. Aleon[2], C. Alexander[3], A. Butterworth[4], S. J. Clemett[5], G. Cody[3], G.Cooper[1], J. P. Dworkin[6], G. J. Flynn[7], M. K. Gilles[8], D. P. Glavin[6], C. Jacobsen[9], G. Matrajt[10], F. Robert[11], M. K. Spencer[12], T. Stephan[13], A. Westphal[4], S. Wirick[9], and R. N. Zare[12], [1]NASA Ames Research Center, [2]Glenn T. Seaborg Institute, [3]Carnegie Institution, [4]University of California at Berkeley, [5]NASA Johnson Space Center, [6]NASA Goddard Space Flight Center, [7]SUNY Plattsburgh, [8]Lawrence Berkeley National Laboratory, [9]SUNY Stony Brook, [10]University of Washington, [11]Muséum National d'Histoire Naturelle, [12]Stanford University, [13]Universität Münster, Institut für Planetologie

Introduction: The primary objective of STARDUST is to collect coma samples from comet 81P/Wild 2. These samples were collected by impact onto aerogel tiles on Jan 2, 2004 when the spacecraft flew through the comet's coma at a relative velocity of ~6.1 km/sec [1]. Measurements of dust impacts on the front of the spacecraft suggest that the aerogel particle collector was impacted by 2800 ± 500 particles larger than 15 μm in diameter [2]. Following recovery of the Sample Return Capsule (SRC) on Jan 15, 2006, the aerogel collector trays will be removed in a clean room at JSC. After documentation of the collection, selected aerogel tiles will be removed and aerogel and cometary samples will be extracted for study. A number of different extraction techniques will be used, each optimized for the analytical technique that is to be used.

The STARDUST Mission will carry out a 6 month preliminary examination (PE) of a small portion of the returned samples. The examination of the samples will be made by a number of subteams that will concentrate on specific aspects of the samples. One of these is the Organics PE Team (see the author list above for team members). These team members will use a number of analytical techniques to produce a preliminary characterization of the abundance and nature of the organics (if any) in the returned samples.

Analytical Techniques: The organic content of collected particles will be investigated by a variety of micro-analytical techniques, with the aim of utilizing individual particles, fragments thereof, and aerogel and Al foil target materials for multiple correlated independent measurements. Characterization of organic matter will include spatial determination of C and heteroatom elemental abundance (synchrotron-Scanning Transmission X-ray Microscopy; STXM), the local chemical environment and redox of carbonaceous phases (C- and O-XANES, EXASF, EELS), functional group identification (e.g., C-OH, C=O, NH_2, etc.) (TOF-SIMS, micro-FTIR/RAMAN), and specific molecular identification of certain classes of organic molecules (HPLC-LIF, μ/ultra-L^2MS, TOF-SIMS). In addition, as part of our effort to characterize potential contaminants, GCMS and LCMS analyses will be made on both returned spacecraft components, and environmental samples collected in the vicinity of the SRC.

Microprobe laser-desorption laser-ionization mass spectrometry, or μL^2MS, will be used for the analysis of polycyclic aromatic hydrocarbons (PAHs) in cometary particles trapped in the aerogel matrix. This technique has been applied extensively to the analysis of low levels (<10^7 molecules) of PAHs in extraterrestrial samples [3,4]. *In situ* spatial analysis of particles in aerogel is possible with μL^2MS, which minimizes the risk of exposing them to terrestrial contamination. This capability also enables the analysis of PAHs in fragmentary debris scattered along particle impact tracks in aerogel.

Similarly, laser desorption/ultrafast ionization mass spectrometry permits identification of specific small to medium (70-2000 amu) size moeities with functional groups susceptible to either resonant or, to a lesser extent, non-resonant, laser ionization [5]. The detection sensitivity for a given molecule is a convolution of parameters - its abundance, its photoionization cross-section, and the instrument response function. Typically this translates to being able to detect tens-to-thousands of molecules in the probed area. Spatial resolution of the instrument is limited to the wavelength of the desorption laser (~10 μm using a CO_2 desorption laser and ~1 μm using a Nd-YAG laser). To provide spatial distribution of specific molecules within a single particle it is necessary to crush the particle into a substrate such as gold so the particle is spread over a larger area. This also provides higher detection sensitivity because the laser desorption is itself inherently a surface process.

TOF-SIMS delivers chemical information on investigated sample surfaces. Atomic, isotopic, and molecular data are gathered simultaneously. Organic molecules can be identified in the mass spectrum either as intact molecular ions or as series of fragments with well-defined mass differences. The latter often allow the identification of entire molecule classes through their characteristic functional groups. Further details on the application of TOF-SIMS in cosmochemistry, also for the analysis of organics, can be found in the literature [6,7].

A new liquid chromatography time of flight-mass spectrometry technique with laser induced fluorescence detection (LCMS-LIF) is now being optimized for the analyses of amino acids and their enantiomeric abundances in individual Stardust grains and aerogel [8]. The search for amino acids in Stardust material will provide important constraints on the nature of carbonaceous meteorite parent bodies and the cometary flux of prebiotic organic compounds delivered to the early Earth.

Scanning Transmission X-ray Microscopes (STXMs) use an intense, monochromatic X-ray beam in the 250-800 eV energy range focused to a <100 nm spot, and detect the intensity of x-rays transmitted by the sample. Raster scanning the sample through the beam produces an x-ray absorption map at a fixed energy. Since the absorption of an element increases sharply at the K-edge, the energy of electron transitions from the K-shell to the continuum, the C-, N-, or O distribution in an ultramicrotome section is obtained by comparing the absorption at energies just above and below the element's K-edge. The result is high spatial resolution C,N,O maps of percent-level light element abundances. Scanning over an energy range spanning the K-edge of an element produces an X-ray Absorption Near-Edge Structure (XANES) spectrum at a sample spot. For different bonding states of a molecule, pre-edge absorptions occur at energies allowing excitation of an electron from the K-shell to a unoccupied molecular orbital. STXM instruments combine high sensitivity, stable background and high energy resolution (~0.1 eV) to resolve features from near-edge spectra. XANES spectroscopy is a sensitive probe of the organic functional groups present in IDPs and meteorites [9].

The two synchrotron microscopes STXM employed for Stardust PET are ALS Beamline 5.3.2, Lawrence Berkeley National Laboratory [10] and NSLS X-1A. These microscopes can combine sub-100 nm mapping capability with high sensitivity, high spectral resolution to produce functional group transects and two-dimensional maps.

Other PE Subteams: In addition to efforts made by members of the Organics PET organics, the study of the returned organics in will also benefit from results of other PE subteams. The Spectroscopy Subteam may well detect spectral features due to organics within the samples. In addition, if any of the organics formed in the interstellar medium or were made from interstellar precursors, there is a chance they will carry D and/or ^{15}N isotopic anomalies [11]. Thus, results from the Isotopes Subteam may bear on our understanding of the origins of some of the organics. The efforts of the various PE subteams will be coordinated by frequent discussions between the Subteam Leaders.

Contamination Control and Assessment: A primary concern for study of organics in the samples will be the issue of contamination. It is very difficult to avoid organic contamination in collected samples and much of the Organic PET's effort will be aimed at establishing the abundance and identity of any contaminants present so they are not falsely identified as being of cometary origin. This will be done by (1) searching for organics on monitoring 'coupons' that were placed with the SRC but not exposed to the cometary flux, as well as coupons exposed during cleanroom operations (2) identifying the organics in air, soil, and water samples taken from the landing site, (3) identifying any organics associated with the SRC ablative heat shields or captured in the return canister's air filter, and (4) characterizing any organics in the original aerogel tiles.

Publication of Results: The Preliminary Examination period lasts for a period of 6 months starting on return of the capsule on Jan15, 2006. PET results will be published in a series of papers in the peer reviewed literature at the end of this period.

Post Preliminary Examination: Upon completion of the PE period, the STARDUST samples will be turned over to the care of the NASA Curatorial Office where they will be made available for study by the entire scientific community. Samples will be distributed in a manner similar to that used for allocating other extraterrestrial samples. More details can be found in another abstract presented at this same conference [12].

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