CHEMICAL ANALYSIS OF WILD-2 SAMPLES RETURNED BY STARDUST. G. J. Flynn[1], J. Borg[2], P. Bleuet[3], F. Brenker[4], S. Brennan[5], C. Daghlian[6], Z. Djouadi[2], T. Ferroir[3], J.-P. Gallien[7], Ph. Gillet[8], P. G. Grant[9], F. Grossemy[2], G. F. Herzog[10], H. A. Ishii[9], H. Khodja[9], A. Lanzirotti[11], J. Leitner[12], L. Lemelle[8], K. Luening[5], G. MacPherson[13], M. Marcus[14], G. Matrajt[15], T. Nakamura[16], T. Nakano[17], M. Newville[11], P. Pianetta[5], W. Rao[18], D. Rost[13], J. Sheffield-Parker[19], A. Simionovici[8], T. Stephan[12], S. R. Sutton[11], S. Taylor[20], A. Tsuchiyama[21], K. Uesugi[22], A. Westphal[23], E. Vicenzi[13], L. Vincze[24], [1]SUNY, Plattsburgh NY 12901 (george.flynn@plattsburgh.edu), [2]Institut d'Astrophysique Spatiale, Orsay, France, [3]ESRF, Grenoble, France, [4]JWG-University Frankfurt, Germany, [5]Stanford Linear Accelerator Center, Menlo Park CA, [6]Dartmouth College, Hanover NH, [7]Lab. Pierre Süe, CEA/CNRS, Saclay, France. [8]École Normale Supérieure de Lyon, Lyon, France, [9]Lawrence Livermore National Laboratory, Livermore CA, [10]Rutgers Univ., Piscataway NJ, [11]University of Chicago, Chicago IL, [12]Institut für Planetologie, Universität Münster, Germany, [13]Smithsonian Institution, Washington D.C., [14]Advanced Light Source, Berkeley, CA., [15]Univ. of Washingrton, Seattle WA, [16]Kyushu University, Hakozaki, Japan, [17]AIST/GSJ, Ibaragi, Japan, [18]University of Georgia, [19]XRT Limited, Port Melbourne, Australia, [20]ERDC-CRREL, Hanover, NH, [21]Osaka Univ., Japan, [22]JASRI/SPring 8, Hyougo, Japan, [23]Univ. of California, Berkeley CA, [24]Ghent Univ., Ghent, Belgium.

Introduction: On Jan. 2, 2004 NASA's Stardust spacecraft flew through the coma of comet Wild-2, capturing dust in low-density silica aerogel for delivery to Earth on Jan. 15, 2006. A description of the capture cells is in Tsou et al. [1]. Wild-2 is a short-period comet, believed to have originated in the Kuiper Belt. Thus, analysis of Wild-2 dust provides the first opportunity to probe conditions in the Kuiper Belt during dust formation and compare them with conditions in the asteroid belt, as inferred from primitive meteorites.

In the ideal case, aerogel capture results in gentle deceleration, giving a conical track with a single terminal particle. However, weak material, e.g., Orgueil, shot into aerogel at ~6 km/s, comparable to the Stardust encounter with Wild-2, frequently leaves many fragments along the track. In addition, the capture results in accretion of a silica coating on the particle [1], suggesting the particle's surface contacted liquid silica, which could mobilize moderately volatile elements.

Some interplanetary dust particles (IDPs) collected from the stratosphere are believed to be cometary [2]. These IDPs are reported to be enriched in moderately volatile elements by a factor of ~3 over CI meteorite composition [3]. Thus, a critical task is to determine if Wild-2 dust is chemically similar to IDPs, to some type of meteorite, or if it constitutes a new type of extraterrestrial material. Modeling by Westphal (Pers. Comm., 2005) indicates that if Wild-2 dust particles show the same compositional variation as the ~10 µm IDPs, it will be necessary to average the compositions of ~30 Wild-2 particles of ~10 µm size in order to distinguish an IDP-like composition from a CI-like composition.

Instruments and Measurements: The Stardust Composition Preliminary Examination Team will employ a variety of instruments in laboratories on 4 continents. X-Ray Microprobes (XRMs), with analysis spots ranging from 10 µm to 200 nm, will perform chemical analyses of terminal particles and map element distribution in 2- and 3-dimensions along tracks in slices and keystones. The inherent limitation on *in-situ* analysis is the escape of fluorescence x-rays, but elements as light as Mg can be detected at the maximum depth reached by 10 µm Wild-2 grains [4]. Some XRMs can perform bonding state characterization by X-Ray Absorption Near-Edge Structure (XANES) spectroscopy and/or x-ray diffraction, identifying mineral hosts of the elements. A proton probe will map element distributions by Proton Induced X-ray Emission (PIXE), Rutherford backscatter spectroscopy and forward scattering ion spectroscopy (which can extend the sensitivity down to H). TOF-SIMS mapping may be done on keystones sliced to expose the track. Particles can be located by optical and tomographic techniques, including electron and x-ray mapping and high resolution x-ray phase contrast imaging. After XRM or PIXE analysis particles will be extracted and ultramicrotome slices will be prepared for XRM and TEM analyses. SEM-EDX and TOF-SIMS will be used to characterize extracted particles. The C and N contents will be measured by EELS and Nuclear Microprobe.

Objectives: During the Preliminary Examination we have five specific science objectives, to determine:

1. if all terminal particles are similar in composition or if they group into distinct compositional types that can be recognized (e.g., by optical characteristics).

2. if the composition of the terminal particle is representative of the particle as it entered the aerogel or if fragments or volatiles were deposited along the track.

3. if the comet contains crystalline grains – olivine, pyroxene, sulfide, carbonate, or hydrated silicate – by combining chemical composition, element speciation by XANES spectroscopy, and x-ray diffraction data.

4. the mean chemical composition of the Wild-2 dust, comparing this to other types of extraterrestrial materials and inferring the minimum temperature in the Wild-2 formation region during condensation.

5. the element associations with mineralogy – testing nebula condensation models.

Results: F. Hörz (JSC) shot dust from Allende and a microprobe standard "unknown" into aerogel cells. Samples of both were provided to each group participating in Stardust chemical preliminary examination, except groups focusing on C and N. Allende provides an indication of the elements each instrument can detect in a chondritic sample while the "unknown" insures consistency in analyses among the laboratories.

Most ~10 µm terminal particles from Allende shots have Ni/Fe ratios significantly lower than the bulk Allende value, suggesting that the ~10 µm terminal particles are not representative of the bulk composition of Allende. Most likely, the terminal particles are dominated by olivine, but we cannot determine if this modification resulted from grinding employed to powder the sample, sieve size separation, shock experienced in shooting the powder, or the aerogel capture process.

Figure 1 shows an Allende entry track extracted as a keystone by Westphal and co-workers [5]. Two-dimensional maps of Fe, Ni, Cr, Cu, and Zn distributions were obtained by Sutton and co-workers using the GSE-CARS beamline at the Advanced Photon Source. The terminal particle has lower Ni/Fe (~0.4xCI) than bulk Allende, consistent with observations on other Allende terminal particles, and very low Zn/Fe (<0.03xCI). In addition to the terminal particle, five other Fe-rich grains along the track were analyzed. The entry hole contains considerable Ni and Zn, suggesting deposition of matrix fragments and/or vapor early in capture, indicating the terminal particle is not representative of the particle striking the aerogel. Simionovici and co-workers at ESRF [6] mapped elements in a terminal particle from the "unknown" shot. Their Ni map shows the elements are not homogeneous in the terminal particle after capture (Fig. 2). They previously found evolution of the oxidation state of grains along a track, suggesting alteration during capture.

Anticipated Complications. While measurement of the chemical compositions of individual particles >0.5 µm in size is relatively straightforward, the ultimate objective of using those data to infer the bulk composition of the non-volatile component of comet Wild-2 will be more challenging. If, as suggested by the captured Allende particles, the residue in the entry hole differs in composition from the terminal particle, it will be necessary to determine the appropriate weighting of the compositions to infer a bulk composition. In addition, particles >150 µm were lost because they penetrate through the capture cell while the smallest particles will be too small for individual analysis.

The most direct approach to determining the bulk chemical composition of Wild-2 dust is to perform bulk chemical analysis of an entire cell, e.g. by ICP-MS or INAA. However, the impurity content of the aerogel itself makes this impossible. If Stardust collected ~1000 particles >15 µm in size, we would expect ~10 particles >15 µm in each cell. The size frequency distribution of Wild-2 dust is not known, but the total mass of Wild-2 dust in a typical cell is likely not to exceed 10^{-6} g. A Stardust aerogel cell weighs ~0.6 g. Tsou et al. [1] found 1800 ppb of Fe in a Stardust aerogel cell by ICP-MS. Assuming CI Fe in Wild-2 dust, all the Wild-2 particles in a single cell are likely to contribute no more than $2x10^{-7}$ gm of Fe while the aerogel contains ~10^{-6} g of Fe. The situation is worse for some moderately volatile elements, which are used to distinguish different types of extraterrestrial materials. If particles contain a CI-level of Zn, the particles in a cell would contain $3x10^{-10}$ g of Zn while the aerogel would contribute $8x10^{-7}$ g. XRM measurements show impurities vary from spot to spot and cell to cell, making background subtraction difficult.

Analysis Plans: The most promising approach to obtaining the bulk composition of Wild-2 grains is to map the distribution of elements along tracks by XRM or PIXE, integrating over all fragments and vapor from the incident particle. We plan to average over all types and sizes of particles and different track morphologies.

References: [1] Tsou, P. et al. (2003) *JGR*, **108**, E10, 3.1-3.21. [2] Brownlee, D. E. et al. (1994) *LPS XXV*, 185-186. [3] Flynn, G. J et al. (1996) in *Phys. Chem. and Dynamics of Interplanet. Dust*, ASP Conf. Ser. 104, 291-297. [4] Flynn, G. J. et al. (1996) *LPS XXVII*, 369-370. [5] Westphal, A. et al. (2004) *Meteor. Planet. Sci.*, **39**, 1375-1386. [6] Simionovici, A. et al. (2006) *Hbk. Practical X-Ray Fluor. Analys.*, Elsevier.

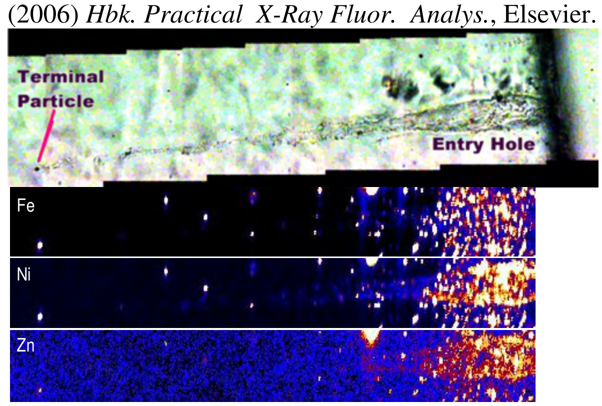

Figure 1: Optical image of an ~865 µm Allende track and Fe, Ni, and Zn maps of the same area.

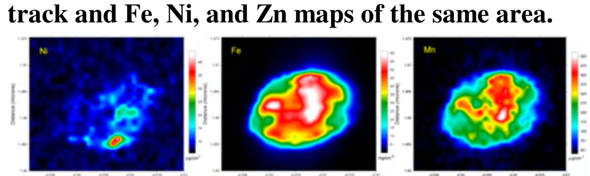

Figure 2: Ni, Fe and Mn maps of terminal particle.