XRD ANALYSES OF SMALL GRAINS USING SYNCHROTRON RADIATION: POTENTIAL APPLICATION TO SAMPLES RETURNED BY STARDUST. D. L. Cook[1], T. Emge[1], G. F. Herzog[1], G. J. Flynn[2], A. Lanzirotti[3], and S. R. Sutton[3,4], [1]Department of Chemistry and Chemical Biology, Rutgers University, 610 Taylor Rd., Piscataway, NJ, 08854 (davecook@rci.rutgers.edu), [2]Department of Physics, SUNY-Plattsburgh, 101 Broad St., Plattsburgh, NY 12901, [3]Consortium for Advanced Radiation Sources, The University of Chicago, Chicago, IL 60637, [4]Department of the Geophysical Sciences, The University of Chicago, Chicago, IL 60637.

Introduction: Crystalline phases are abundant among the samples that the Stardust mission collected from the coma of comet 81P/Wild 2 [1,2]. Due to the small size and high value of the samples, highly sensitive and non-destructive analytical methods are needed for petrographic characterization. Methods applied to date include scanning electron microscopy (SEM), transmission electron microscopy (TEM), conventional microscopy, x-ray fluorescence (XRF), and time-of-flight secondary ion mass spectrometry (TOF-SIMS) [1-3]. At this writing, 16 minerals have been identified in Stardust samples [2]. We discuss here one way to apply synchrotron x-ray diffraction (SXRD), a method of extremely high sensitivity, to Stardust samples.

We were motivated by technical considerations. Previously, nuclear reaction analysis (NRA) was used to determine carbon and nitrogen abundances in three intact Stardust grains [4]. NRA requires that samples be mounted vertically in a conductive medium, and indium foil was chosen for this purpose. Although, several additional methods of analyses can be performed on samples pressed into indium foil [4], a shortcoming is that samples are then difficult to remove, and the presence of indium hinders the application of standard petrographic methods (*e.g.*, TEM).

SXRD has been used to identify phases present in small (10 to 35 μm) interplanetary dust particles (IDP) captured in IDP collectors [5]. We set out to investigate whether synchrotron radiation can be used to perform XRD on small samples pressed into indium foil. For this purpose, samples of San Carlos olivine and bulk samples of the carbonaceous chondrites Murchison and Tagish Lake were chosen; carbonaceous chondrites are known for their fine-grained and complex mineralogy [*e.g.*, 6-8]. Two additional goals were to determine if the indium foil thickness affects the quality of the measurements and/or the ability to make them.

Samples and Methods: San Carlos olivine was crushed with an agate mortar and pestle. Bulk samples of Murchison and Tagish Lake were both ground lightly with an agate mortar and pestle. Two grains each of San Carlos olivine were pressed into indium foils of three different thickness (25 μm, ESPI; 50 μm and 100 μm, Alpha Aesar); foil purities are $\geq$ 99.99%. In addition, one particle each of Murchison and Tagish Lake was pressed into the 25 μm foil. Grain sizes ranged from ≈ 45 to ≈ 70 μm in diameter. The foils were attached to an empty 35 mm slide frame for SXRD analysis.

Sample analyses were conducted at beamline X26A of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory using monochromatic x-rays (17.374 keV) focused to a 5 × 9 μm spot using Kirkpatrick-Baez focusing mirrors. Data were acquired over a 60-second period and were collected using a Brucker SMART 1500 CCD system. The samples were not rotated during data collection. An analysis of a nearby portion of each of the three indium foils sans grains was also made.

Results and Discussion: Data reduction was performed using the Fit2D software package. Calibration of the camera distance and the x-ray wavelength were made using data from analyses of two standards during the analytical session. Corrections were also made for detector tilt and rotation. Alpha-corundum (Al_2O_3) from the NIST X-Ray Powder Diffraction Intensity Set (SRM 674a) was used for high 2-theta values, and silver behenate ($AgC_{22}H_{43}O_2$) was used for low ones. Mineral identifications were made using the search-match software JADE.

The XRD patterns (intensity versus 2θ) from the integration of the SMART 1500 area detector images of the three indium foils are shown in **Figure 1**. The peak at 15.1 degrees (2θ) is due to the (101) reflection and can be quite intense depending on whether the bulk sample is oriented near the Bragg condition. In particular, replicate analyses of the 50 μm foil illustrate the strong effect of sample orientation on the 15.1 degree peak intensity. For one analysis, the peak intensity is ≈ 700 a.u., whereas this peak is absent from the second analysis. In future experiments, it may be possible to orient the foil such that the peaks from indium are avoided. In the eight grain analyses we performed, usually only the (101) indium peak is observed, and it is narrow enough not to interfere with the identification of sample peaks that are in the same region.

The integrated XRD patterns of the indium foils also reveal several analytical artifacts. Effects of uncertain scaling of data from the corners of the rectangular

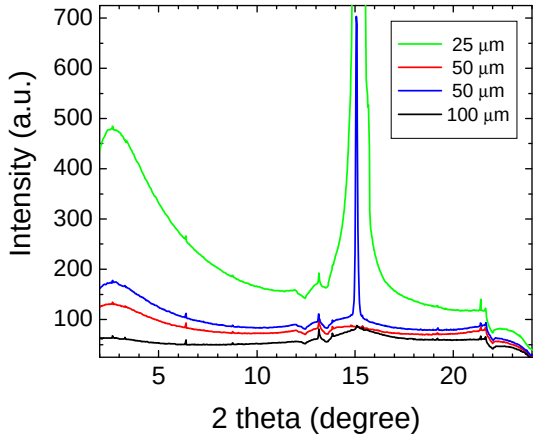

Fig 1: Integrated XRD patterns for the three indium foils of varying thickness. The peak intensity from the 25 μm foil is 3009 a.u.

images in Fit2D or at the junctures of CCD elements occur as "v" shaped dips at 12.5, 13.5, and 22 degrees. The integrations also show bad pixel effects (*i.e.*, sharp spikes at 6.4, 13.2, 13.8, 19.1, 21.3 and 21.6 degrees). The latter are easily distinguished from sample peaks because of their extreme narrowness.

One of the two olivine grains pressed into the 25 μm foil produced an observable XRD pattern. The integrated XRD pattern for this particular sample contains peaks with d-spacings characteristic of both olivine and indium metal as expected. For the other five olivine samples, only the peak(s) for indium metal is/are present. Absorption by the foil of the olivine diffraction from each of these five grains may explain the absence of olivine peaks in the integrated patterns. For the one 25 μm foil sample that did not yield any olivine diffraction, it is possible that grain was not imbedded as deeply into the foil as the grain that produced a pattern. Hence, the minimum useful foil thickness may be slightly less than 25 μm. Alternatively, these olivine crystals may have been in an orientation that produced no strong Bragg diffraction onto the detector.

Analyses of both Murchison and Tagish Lake produced XRD patterns comprising multiple rings. The d-spacings in the integrated pattern for Murchison show that the major component is most likely cronsteditite $[Fe_3(Si,Fe)_2O_5(OH)_4]$, which accounts for all of the observed peaks (except for one due to the indium foil). However, the presence of magnetite cannot be excluded because its peaks are all concealed by cronstedtite. The integrated XRD pattern for the Tagish Lake sample is shown in **Figure 2**. The presence of several minerals is likely for the Tagish Lake sample, as no single mineral dominates the XRD pattern. The most likely components are magnetite, olivine, and chlorite; two small peaks were not indentified. For both carbonaceous chondrite samples, the small quantity of sample used and the lack of sample rotation preclude the determination of relative quantities of the matched phases and also preclude the identification of minor (< 5%) phases.

Identification of phases in both carbonaceous chondrites demonstrates the potential to perform XRD analyses of small, multi-component samples pressed into indium foil. Analysis of smaller samples (*i.e.*, ≈ 10 μm) may be possible using this technique, which could be applicable to larger Stardust samples. Rotation of samples during analysis and/or longer acquisition times could be used to improve mineral identification in small or weakly diffracting samples.

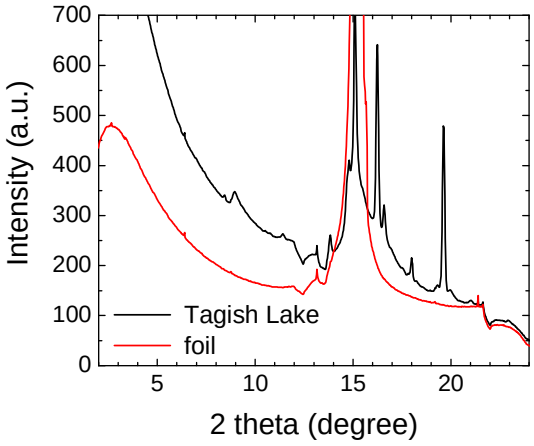

Fig 2: Integrated XRD pattern for the Tagish Lake sample pressed into 25 μm indium foil. The pattern for the indium foil is shown for comparison.

Acknowledgments: We thank William Rao at the NSLS for assistance with the experimental setup and data acquisition. The XRD facility at X26A was funded by NASA SRLIDAP grant NAG5110-4 (to G.J.F.)

References: [1] Brownlee D. et al. (2006) *Science*, *314*, 1711-1716. [2] Zolensky M. et al. (2006) *Science*, *314*, 1735-1739. [3] Flynn G. J. et al. (2006) *Science*, *314*, 1731-1735. [4] Herzog G. F. et al. (2007) *MAPS*, submitted. [5] Flynn G. J. et al. (2000) *LPSC XXXI*, Abstract #1772. [6] Bunch T. E. and Chang S. (1980) *GCA*, *44*, 1543-1577. [7] Zolensky M. et al. (1993) *GCA*, *57*, 3123-3148. [8] Zolensky M. et al. (2002) *MAPS*, *37*, 737-761.